THE SYNTHESIS OF BORON CARBIDE FILAME

FINAL REPC

SPACE SCIENCES
LABORATORY

Prepared for National Aeronautics and Space Administration Under Contract NASw-670

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Final Report

by

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July 1964

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SUMMARY

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A contract for the National Aeronautics and Space Administration, number NASw-670 has been granted to synthesize B_4C whiskers and determine their strength, crystal structure, and potential in forming high strength composite materials. This is the final report of that contract.

B_4C whiskers have been grown successfully both by evaporation from pure B_4C vapor and by a chemical method based on the flow of appropriate gases over a heated substrate. Thus far, the best whiskers are being produced by the former method. The largest whiskers grown to date average 1 cm in length. The latest growth studies include combinations of both methods in an attempt to optimize the process as it is now used.

A major effort has been to measure the room temperature properties of a number of representative B_4C whiskers. The strongest crystal to date supported a stress of 965,000 psi in tension. A modulus value of about 65×10^6 psi has been determined. Studies on the morphology, orientation, crystal structure, etc. of B_4C whiskers have paralleled the strength and growth work and is reported here. Thus far only the "A" type whiskers has been found. Wetting studies conducted in both vacuum and hydrogen atmosphere served as a screening test in selecting a suitable metal for metal-B_4C composite fabrication. Fernico "5" was the obvious choice for future work. These results will be described. Epoxy based composites have been fabricated and tested in tension. A factor of four in strengthening was achieved with short fiber reinforcement. A tensile value of 24,700 psi was measured for a 10 volume percent composite. Unreinforced epoxy averaged 6000 psi in tension.

A description of the experimental equipment used will be presented. Included in this final report is a short history of whisker growth and their properties in general. The expected advantages whish could be realized when B_4C whiskers are effectively utilized in composites are discussed.

author

I. INTRODUCTION

The severe thermal and stress problems associated with space applications has limited large advances in the design and efficiency of engineerin structural materials. A dire need exists for high strength, high modulus, light weight materials for space structures. An approach to a solution of the space materials problem s pertains to tension structures in particular, would be the use of composite materials which could exhibit properties that no single material possesses alone. It has been deduced[1] that significant reduction in weight (as much as 80%) could result if ultra-strong filaments could be utilized in a composite material. Experience has already been gained with alumina whiskers* embedded in silver. Such composites have been tested at 1600°F, which is 94% of the melting point of silver. These materials were found to withstand an 82,000 psi tensile stress. A urther advance in high strength silver composites, as an example, could be achieved if B_4C whiskers were available. B_4C combines a high melting point with a high modulus of elasticity and low density. It therefore has a very high potential strength-to-weight and modulus-to-weight ratio, greater than any material previously considered. Pertinent data to illustrate this fact are presented in Table I. In Figure 1 is presented a strength-versus-test temperature curve for α-alumina whiskers as was determined by Brenner.[2] B_4C, because of similar modulus of elasticity but high melting point, would be expected to have similar room temperature properties, but its elevated temperature strength probably would not drop as rapidly. For example, B_4C whiskers should retain significant levels of strength to nearly 4500°F, whereа α-Al_2O_3 whiskers retain their strength to about 3700°F. Thus, B_4C potential offers substantial improvemei (about 40 percent) over α-Al_2O_3 as a material for strengthening composites at high temperature.

Table I lists the densities, moduli of elasticity and melting points for a number of refractory metals and compounds. As can be noted, B_4C has the highest modulus/density ratio of any material listed.

*Naval Bureau of Weapons Contract NOw 60-0465d[16]

TABLE I

DENSITIES, MODULI OF ELASTICITY, AND MELTING POINTS FOR A NUMBER OF REFRACTORY METALS AND COMPOUNDS (AFTER HOFFMAN, Ref. 1)

Material	Chemical Symbol	Density (lb/in^3)	Modulus of Elasticity at $70^\circ F$ (psi $\times 10^{-6}$)	$\left[\frac{\text{Modulus}}{\text{Density}}\right]$ (in. $\times 10^{-8}$)	Melting or Decomposition Temperature ($^\circ F$)
Beryllium	Be	0.066	44	6.65	2340
Boron	B	0.083	50	6.03	4200
Molybdenum	Mo	0.0369	52	1.41	4800
Tungsten	W	0.697	52	0.74	6170
Tantalum	Ta	0.601	27	0.45	5450
Columbium	Cb	0.310	23	0.74	4400
Aluminum Oxide	$\alpha - Al_2O_3$	0.137	52-74	3.8-5.4	3660
Beryllium Carbide	Be_2C	0.088	45	5.08	3800
Beryllium Oxide	BeO	0.103	55	5.33	4580
Boron Carbide	B_4C	0.091	65	7.15	4500
Magnesium Oxide	MgO	0.129	12	0.93	5070
Molybdenum Carbide	Mo_2C	0.320	33	1.03	4870
Silicon Carbide	SiC	0.115	70	6.10	4350
Silicon Oxide	SiO_2	0.083	11	1.32	3150
Tantalum Carbide	TaC	0.523	42	0.80	7020
Titanium Carbide	TiC	0.178	51	2.85	5700
Titanium Oxide	TiO_2	0.170	14	0.82	3330
Thorium Oxide	ThO_2	0.346	21	0.61	5900
Tungsten Carbide	WC	0.567	102.5	1.81	5030
Zirconium Carbide	ZrC	0.242	49	2.02	6400
Zirconium Oxide	ZrO_2	0.193	36	1.87	4700
Zirconium Silicate	$ZrSiO_4$	0.154	24	1.56	4600

A. OBJECTIVES AND APPROACHES

1. Growth

The development of high strength B_4C whisker reinforced composites cannot be achieved without an adequate supply of reproducibly high strength whiskers. Therefore, a systematic study of the growth parameters for this material was conducted. The specific approach was that of studying the formation of B_4C whiskers by the two aforementioned vapor methods and a combination of these. By far, the best B_4C whiskers to date have been made using the pure vapor technique.

Although whiskers can be produced from the pure vapor, a process based on a chemical reaction in the vapor state would be advantageous from the standpoint of the lower reaction temperatures involved, higher deposition rates (because of potentially higher operating pressures) and more precise

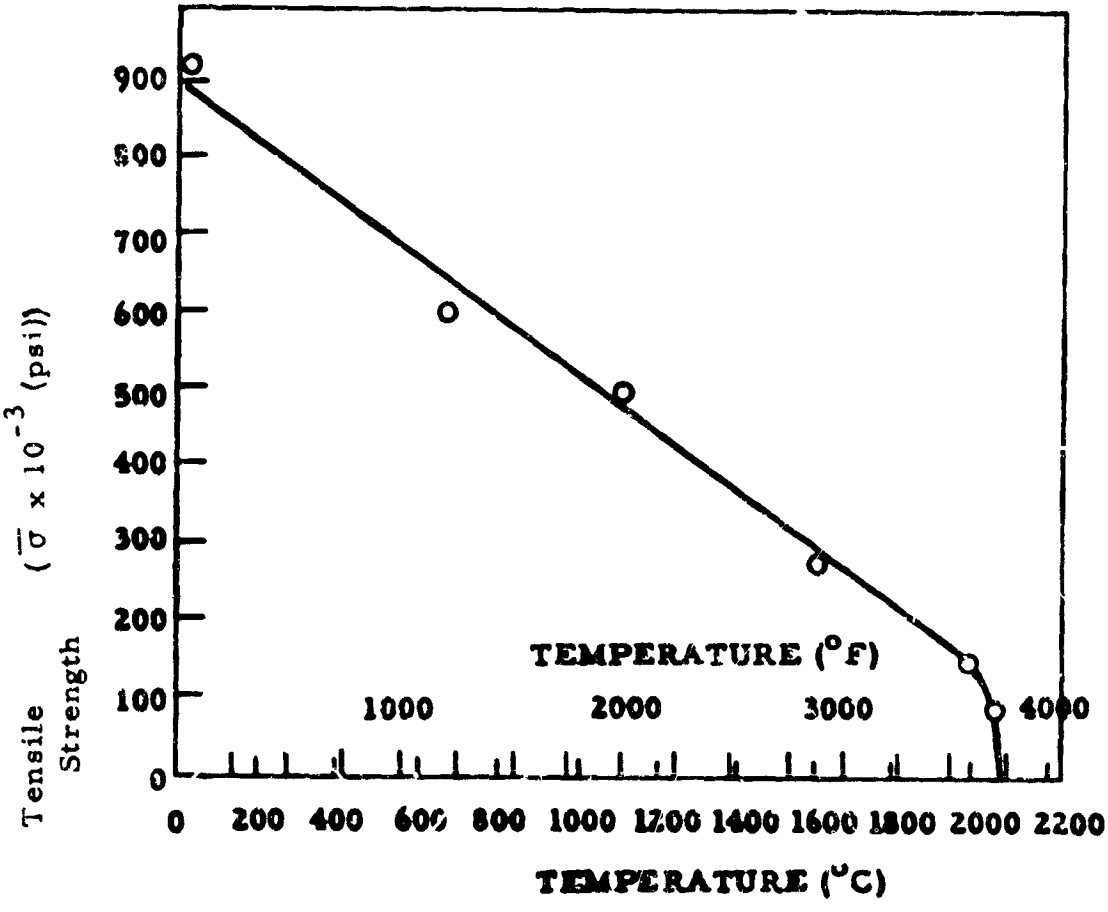


Figure 1. Average Tensile Strength of α-Al_2O_3 Whiskers

control of the gaseous species. Therefore, the chemical method which involves the simultaneous flow across a heated substrate of various gases (containing the essential components necessary to produce the final stoichiometric B_4C) was studied. Because the dynamic method has many process variables, much experimentation would be required to establish optimum growth conditions. Thus far, only limited success has been achieved. Therefore, the pure vapor deposition method for growing B_4C whiskers was used as a means of accumulating a supply of B_4C whiskers. This method has been optimized so that enough whiskers are grown with each run to make one or two micro-composites.

A third method studied was the combination of the dynamic and pure vapor techniques. Such a combination could be useful if nucleation in the dynamic system is difficult and specific impurities in the pure vapor method are important. No definite conclusions were arrived at with more work on this approach being contemplated. The strength characteristics of B_4C whiskers as a function of such variables as whisker orientation, diameter, temperature, etc. are necessary in order to predict composite strengths and to eventually fabricate strong useful composites.

2. Strength

Strength studies have been pursued with the objective of measuring the tensile properties of B_4C whiskers at room temperature. Since size, orientation and perfection effects can be expected, the approach has been to test random specimens of varying concentration and length. The tested specimens are then classified by metallographic and x-ray techniques and the variables in structure which are detected are correlated with strength data.

3. Structure

Studies on the morphology, orientation, crystal structure, etc. have supported and extended the strength studies and also add to our basic scientific knowledge of fibrous composites. Former tensile specimens have been classified as to orientation, structure, perfection, etc. by the utilization of techniques such as electron microscopy, etc.

4. Composite Studies

The final objective is the fabrication of composite structures containing B_4C whiskers. The goal of the composite study is the utilization of strong whisker components into large useful structural members. It is the phase which can justify the interest and work expended in this field and carries with it the promise of future super-tailor-made materials. Wetting experiments have been performed using the sessile technique for determining the wetting properties of various metals on bulk B_4C. These studies are necessary in order to choose a metal matrix material which can bond well to B_4C without harmful reactions taking place. Also some micro-composites have been fabricated using an epoxy-based plastic containing B_4C whiskers.

The present effort has been successful in growing B_4C whiskers routinely. The whiskers are of sufficient size so that handling for subsequent strength and composite studies has not proved a difficult task. Individual whiskers have also been studied metallographically utilizing high optical magnification and electron microscopy and applicable x-ray techniques. A small number of composite structures of B_4C whiskers in epoxy resin have been fabricated and tested.

II. WHISKER BACKGROUND

It has been demonstrated that the reinforcement of a metallic matrix is possible through the use of non-metallic whiskers. There are several properties of whiskers which make this possible. Foremost is their phenomenal strength and relatively low density. Values of tensile strength may be as high as 6×10^6 psi depending upon the element or compound considered.

A. THE NATURE OF WHISKERS

A scientific curiosity for many years, the filamentary crystal (whisker) is now being evaluated as a potentially useful structural material. Silver hairs which are whisker-like growths were reported by Ercker[3] in 1574. It is interesting to note that the descriptive nomenclature for fine, hair-like crystal forms--whiskers--is somewhat unscientific but most appropriate. The discovery by Galt and Herring[4] in 1952 that tin whiskers possessed tensile strength approaching theoretical values (strength values unattained by crystalline materials prior to this time) took the whiskers from the mineralogist's curio box to the laboratory. The interest generated in whiskers has brought about much valuable knowledge and many contributions to the fields of crystal growth mechanisms and of the strength of solids.

A distinction can be made between whiskers according to their origin. Whiskers can be grown from a melt; from supersaturated gas phases; from supersaturated liquid phases; from solutions; from chemical decomposition; by electrolysis or by growth from the solid. The "proper" whisker grows by the migration of atoms to the whisker base without passing through another phase (solid - phase growth). "Proper" whiskers are believed to form by surface migrations or the diffusion of atoms along a dislocation. Although many of the above modes of growth do not produce whiskers without phase change, the crystal perfection, defect structures and properties can be similar. A discussion of the many systems which produce "proper or other whiskers together with postulated growth mechanisms is not contemplated here, although many such studies and reviews are presented in contemporary scientific literature.

The morphology or form which a whisker may take can vary greatly. Shapes described as "kinked", "spiralled", "twisted", "hollow", etc have been reported. However, the high strength whiskers of most practical interest are solid and straight, with a large length-to-diameter ratio and a high degree of surface perfection. Whisker diameters can vary from submicron size to many thousands of microns and the whiskers may be many centimeters in length. Most whiskers are single crystals with their principal geometric axis parallel to a prominent crystallographic direction.

Most tensile strength determinations have been made on straight specimens. In general, as seen for alumina whiskers (Figure 2), the strength of whiskers increases as the whisker diameter decreases. The strength of whiskers has been found to be 100 to 1000 times stronger than larger bulk crystals of the same composition. One prominent theory of whisker strength is dependent on the degree of crystal perfection possible in such micro-crystals. Variations of strength between whiskers can then be rationalized by postulating slight differences in crystal and surface perfection, purity, surface films, etc.

Studies on the growth and properties of whiskers is a subject of much current interest. Much data are being accumulated but the variations of growth systems and growth conditions appear endless, so a great deal remains to be learned regarding the kinetics and mechanisms of whisker growth. However, studies are being conducted to investigate process variables whereby whiskers can be grown in sufficient quantity and quality.

B. GROWTH OF WHISKERS

1. Growth Mechanism

A widely accepted mechanism of whisker growth is attributed to Sears[5]. By applying the dislocation theory of crystal growth[6], he proposed that whiskers contain a screw dislocation along the crystal axis which emerges at the tip. The whisker extends in length by the addition of atoms to the protruding terminal of the screw dislocation while maintaining smooth lateral surfaces. The Sears hypothesis contains the following criteria

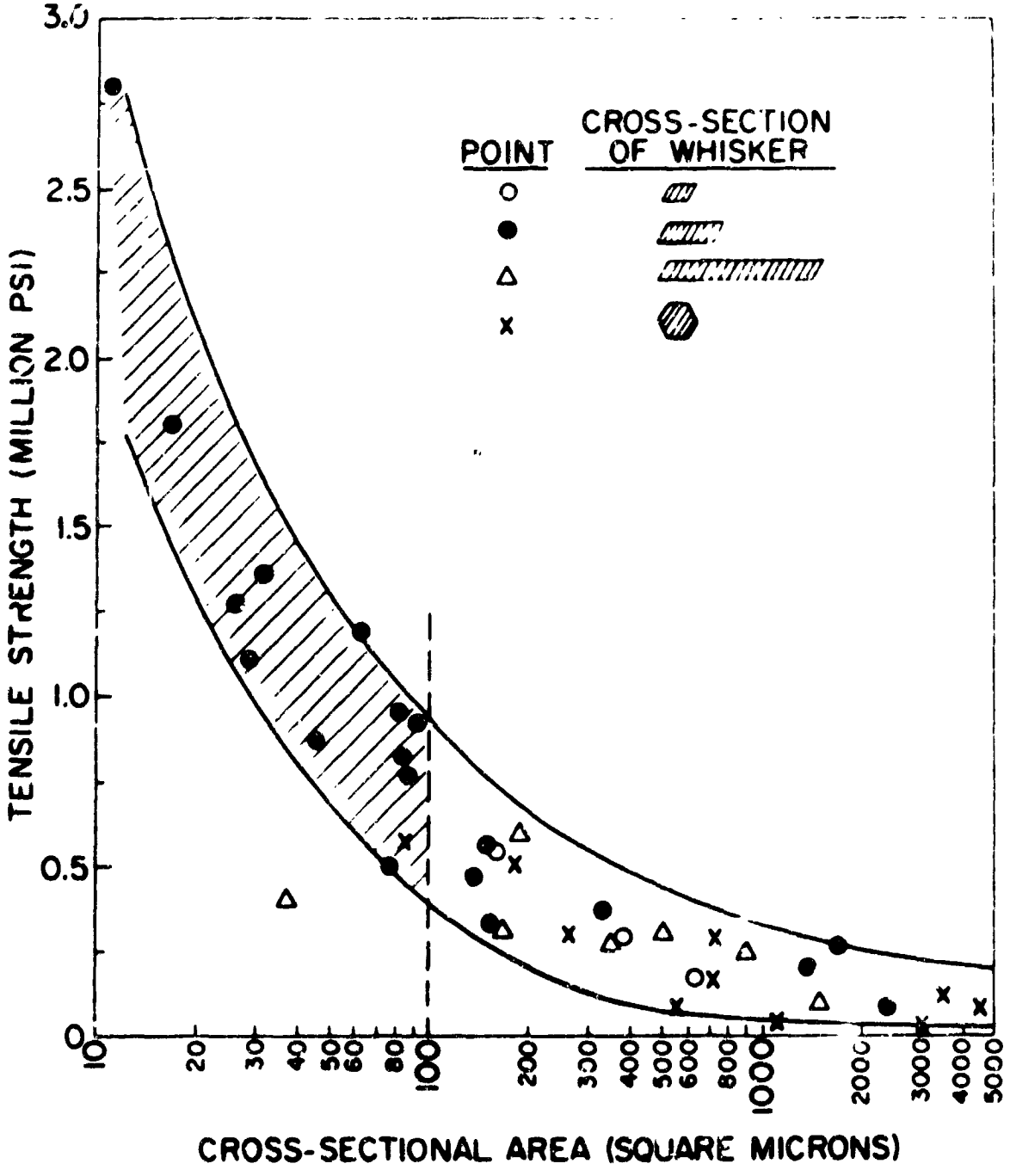


Figure 2. Relation Between Tensile Strength and Cross-Sectional Area of α - Al_2O_3 Whiskers

(a) that only one screw dislocation is present parallel to a major crystal axis and (b) during growth, the crystal is unable to nucleate new layers on its lateral surfaces due to insufficient supersaturation of the vapor.

Sears[7] has shown that the critical supersaturation criteria is valid for the growth of whiskers, from the vapors of the following materials: mercury; silver; zinc; cadmium; and calcium sulfide. Indirect evidence of the presence of screw dislocations within various whiskers has been presented by others, most notably by Webb and Forgeng[8] for alumina whiskers.

There are, however, many experimental observations which are inconsistent with the Sears hypothesis. Notable among these are (a) the need for specific surface activated impurities toproduce small diameter high surface perfection whiskers[9], (b) the presence of steps on the surfaces of the whiskers as indicated by their tapers and overgrowths[9] and (c) the absence of the elastic twists in most whisker materials as would be required for the presence of axial screw dislocation[10]. The presence of steps suggests that their generation is not the rate limiting process in their growth and the absence of the elastic twist would require a much more elaborate dislocation network if dislocation growth is involved. Additional critical experiments will be required before the exact mechanism of whisker growth from the vapor can be understood.

The growth of B_4C whiskers in the present study was accomplished utilizing the technique developed by Sears for his studies of growth mechanism The essential features of the growth experiments are divided into two approaches; namely, (1) growth by the vaporization of bulk B_4C and (2) growth by the dynamic flow of gases containing the atomic species essential to the formation of B_4C. There are other methods which could conceivably be used to grow B_4C whiskers.

C. WHISKER APPLICATIONS

Refractory inorganic single crystal whisker materials have such phenomenal strength and thermal stability at elevated temperatures that, depending on cost and availability, they will probably find many applications

in rockets and missiles, nuclear reactors, supersonic jet aircraft and other types of military weapons and space vehicles (it is not intended to imply that military applications would necessarily be the only potential for whiskers). The main potential use for whiskers is for the reinforcement of metals, plastics and ceramics for both low and high temperature applications. Certain whisker materials, such as the refractory oxides, are usable as heat insulators; other whisker materials may qualify as special liquid and gas filters, and for use in instruments. With whisker composites, it appears reasonable that structural materials may be developed which possess an order of magnitude increase in tensile properties compared with the best materials available today, (for use in both ambient and elevated temperature applications). Critical applications other than those of reinforcement may some day also become important, if the problems of availability and cost are solved.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. GROWTH STUDIES

1. Description of Equipment

Two high temperature resistance heated vacuum furnaces with subsequent modifications have been used on this program. These furnaces are of a unique design that provides long, very uniform (with ± 5°C) hot zones at temperatures up to 2400°C.

The larger of these two furnaces (Figure 3) has a hot zone 4-1/4" in diameter by 9" long and the furnace is pumped by a 50 c.f.m. Welsh Model 1398 mechanical pump. This pump can evacuate the furnace to a pressure of less than 1 micron (10^{-3} Torr) as monitored by a Pirani gage. The graphite heating element of this furnace is operated at low voltage and high amperage by a combination of transformers controlled by a saturable core reactor. The element is insulated with graphite felt and the entire outer jacket of the furnace is water cooled. Two quartz viewing ports, one on the top and one on the side of the furnace, allow observation of the inside of the furnace and the outside of the heating element respectively. The temperature is monitored with an optical pyrometer.

The smaller of the two furnaces (Figure 4) has a hot zone 1-3/4" in diameter by 7" long, and is pumped by a 5 c.f.m. Welsh mechanical pump. This furnace is similar to the one described, except that it is smaller. The small furnace is provided with rotometers, valving and manifolds to allow combinations of gases to be admitted to the furnace during operation. It also has a high temperature boiler pot to facilitate the introduction of less volatile compounds to the furnace.

An adapter was later designed and constructed so as to provide for the stacking of two small vapor deposition furnaces one on top of the other, (Figure 5) with a continuous deposition tube extending through both units. This arrangement allows for the operation of two distinct nine inch temperature zones with a minimum of transition temperature area. At first this furnace was plagued with a distinct narrow cold zone at the transition

Figure 3. Large Graphite Resistance Heated Furnace with Hot Zone 4 1/4" Diameter by 9" Long. (about 1/8 actual size)

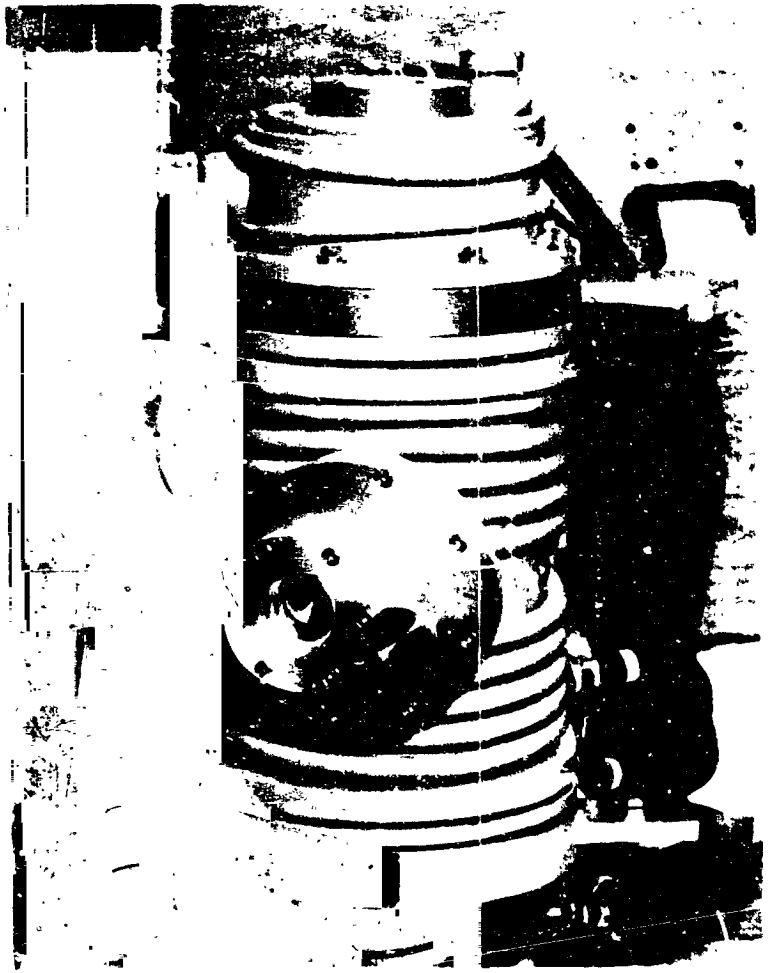


Figure 4. Smaller Graphite Resistance Heated Furnace with Hot Zone 1 3/4" Diameter by 7" Long. (about 1/4 actual size)

point between the two heat zones, however improvements of the internal design have greatly minimized this problem. This furnace permits close control of temperature and pressure parameters necessary to the experimental studies.

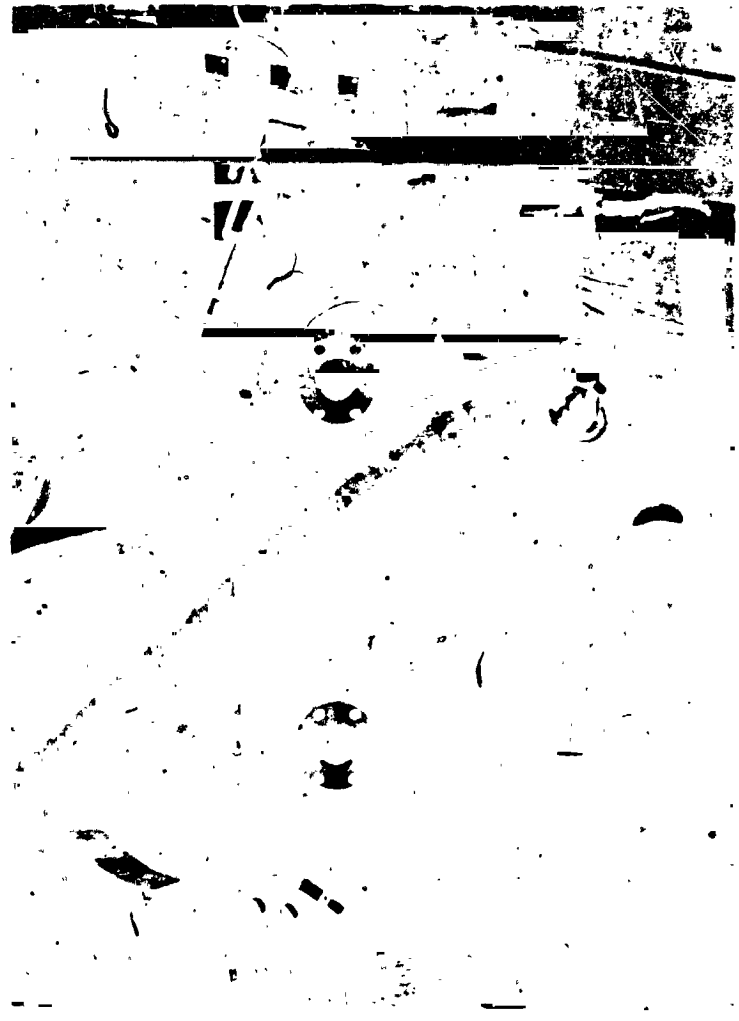


Figure 5. Stacked Furnace Assembly.
(about 1/8 actual size)

2. Growth of B_4C Whiskers

The furnaces described above have been in constant use on the investigation of boron carbide whisker growth. Three growth methods have been partially evaluated: (1) the pure vapor method, (2) a modification of the pure vapor method utilizing a carrier gas, (3) and the chemical method.

a. The Pure Vapor Method

In this method boron carbide is vaporized, and then recondensed in the form of whiskers. The first configuration used with this method utilizes at the bottom of the large furnace, a 1" inside diameter by 3/8" deep ATJ graphite cup filled with boron carbide powder (Fisher Scientific Co., -320 mesh) placed on a pedestal 2 inches into the hot zone. An ATJ graphite deposition mandrel (Figure 6) 3" in diameter by 9" long reduced to a 1-3/4" diameter by 5-1/4" long chimney was placed over the cup in the furnace. The chimney section extends out of the hot zone and hence provides a temperature gradient at the upper end of the furnace. Typically, when the furnace is operated at 1900°C, the temperature in the bottom one inch of the chimney section is 1700°C thus providing a cooler area for the deposition of the B_4C vapor (evaporated at 1900°C). During a typical run in which B_4C whiskers are grown, the furnace pressure is approximately 75 microns. The effect of temperature on the growth process is critical. A fifty degree change in furnace temperature can appreciably alter the length and population density of the boron carbide whisker product. The original vaporization crucible (2.5 cm diameter) provided approximately 5 cm^2 of vaporization area. A new boron carbide "crucible" was constructed from ATJ graphite in the form of a "Lazy Susan", that is, six concentric trays of diminishing diameter were supported on a central rod of graphite (Figure 7). This provided a crucible area of 80 cm^2 for the vaporization process. Micron lengths of boron carbide whiskers were obtained in using the original crucible, while whisker lengths of about one millimeter were obtained in using the new crucible. A second, fifteen tray "Lazy Susan" (Figure 8) with a tray area of approximately 180 cm^2 was constructed which now filled most of the vaporization section of the furnace.

The optimum furnace conditions at present are: 5 hour duration furnace heats, with a temperature of 1900°C in the vaporization area and approximately 1700°C temperature in the whisker deposition area. Physically the "Lazy Susan" is supported 1-1/2" above the furnace bottom allowing the

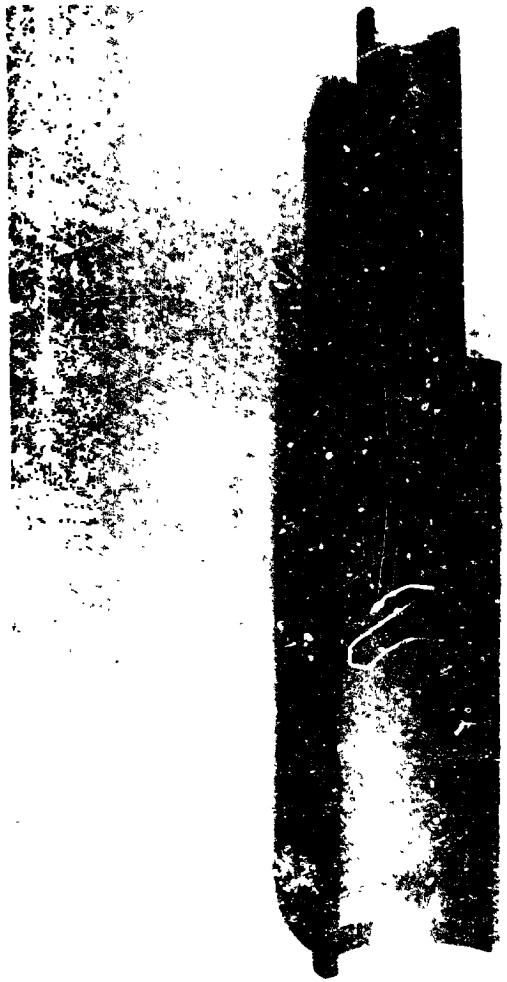


Figure 6. Sectioned Deposition Mandrels from Large Furnace. (about 1/4 actual size)

Figure 7. Initial "Lazy Susan".

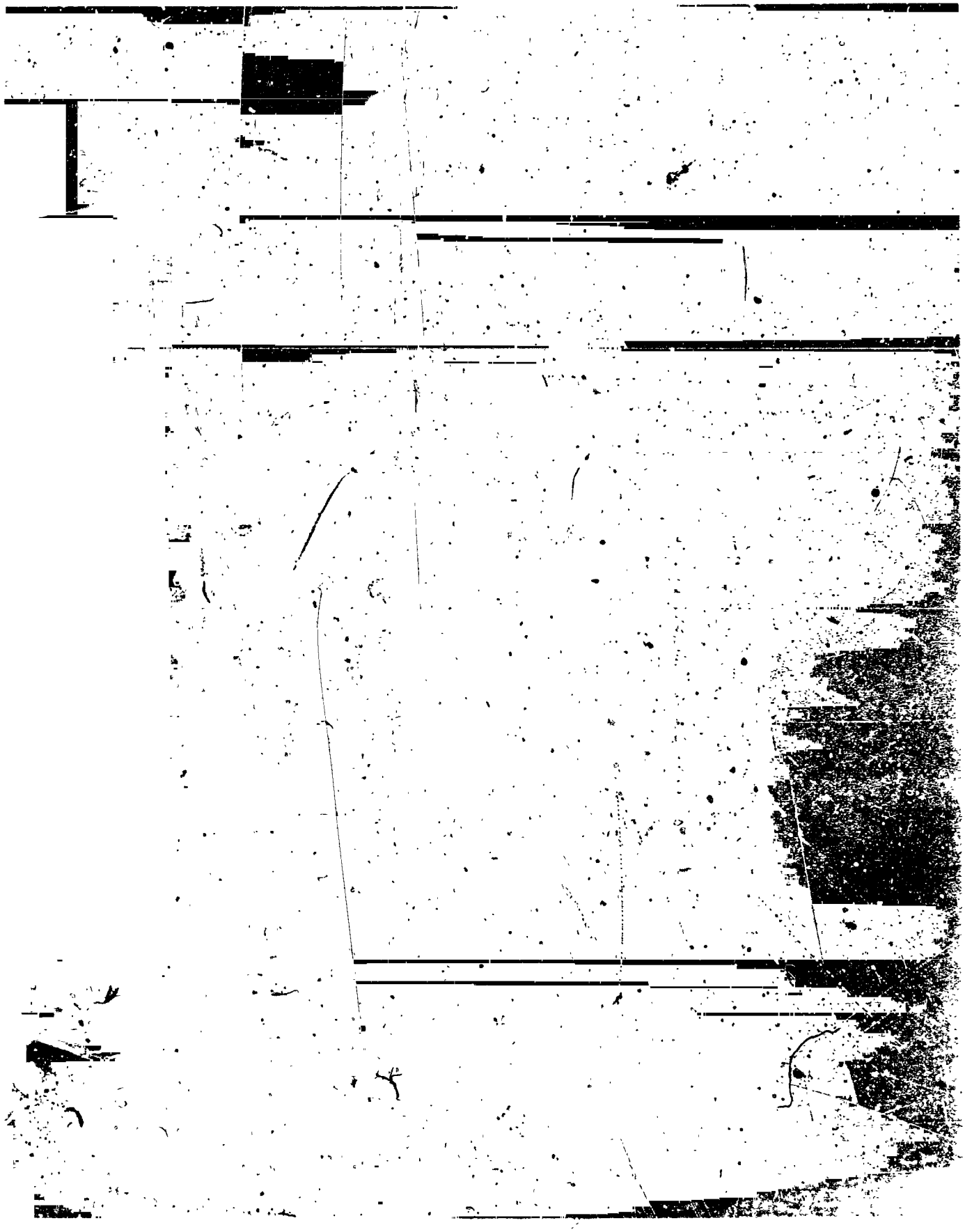


Figure 8. Large "Lazy Susan" including Main Deposition Mandrel with Adaptor Ring - Actual Size.

top two trays of boron carbide to extend into the chimney section of the deposition tube. Figure 9 shows whiskers on the edge of the adapter ring of a deposition mandrel. The growth region extends approximately four centimeters into the chimney of the deposition mandrel. By increasing the amount of B_4C placed in a large "Lazy Susan" type material tray from approximately 20 grn to more than 70 gms in present runs and by using the large vapor deposition furnace, the population density and the average length of the B_4C whiskers produced has been greatly enhanced. For example, the maximum whisker lengths have increased from 5 mm to ~ 20 mm as a result of the increased amount of B_4C "Lazy Susan" trays. Figure 10 shows a typical growth in a section of the deposition area. Optimum furnace conditions have remained the same, (i.e., 5 hours heat at 1900°C in the vaporization area). An increase in whisker length can be obtained by increasing the run time in the large furnace to 7.5 hours, however, this produces surface overgrowths on a significant number of whiskers. Figure 11 shows an example of such an overgrown whisker.

An ATJ graphite "Lazy Susan" shown in Figure 12 together with the double length reaction tube, was constructed for the stacked furnace. When loaded with up to 15 gm of B_4C powder this furnace grows the same quality of whiskers as the large furnace. For a time, due to the short cool zone existing at the junction of the heating elements, all the whisker growth occurred at the point of lowest temperature so that the vapor did not reach the upper furnace. This is well illustrated in Figure 13. After modifying the furnace design, the cool zone was virtually eliminated and whisker growth proceeded on upward into the top furnace. The supply of B_4C vapor provided by the "Lazy Susan" is inadequate, however, to produce many long whiskers over such an increased area in a reasonable time. Although similar results have been obtained in both furnace geometries (i.e., large furnace vs. small stacked furnaces), the operating conditions are not identical. The small furnace requires a temperature of 2100°C in the evaporation zone compared with 1900°C in the large furnace. Deposition

Figure 9. Boron Carbide Whiskers on Deposition Tube Adaptor Ring - 5X.

Figure 10. Typical Growth of B_4C Whiskers at 25X.

Figure 11. Photomicrograph of "Overgrown" B_4C Whisker at 650X.

Figure 12. "Lazy Susan" Tray and Deposition Tubes Used in Stacked Furnace

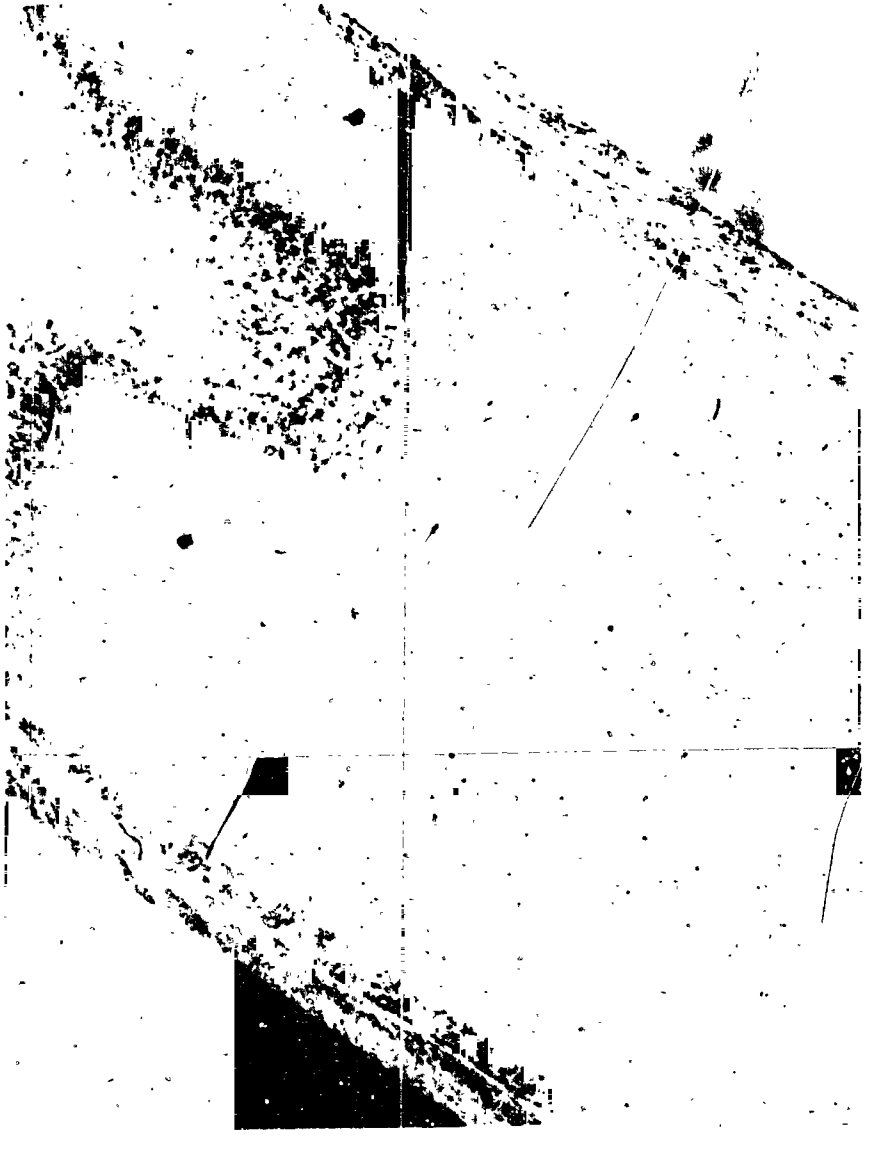


Figure 13. Illustration of Effect of Cool Section in Deposition Tube - 5X.

zone temperatures do appear to be similar, however, and are approximately 1700°C. Recent experiments with the modified method of operation using a carrier gas suggest that the deposition temperature in the stacked furnace should be lowered slightly.

b. Pure Vapor Method with Carrier Gas

Since the supply of B_4C vapor by vaporization under a vacuum was inadequate for the growth of long whiskers over a large area, in the stacked furnace, it was decided to try to improve the vapor supply by running a small flow of hydrogen as a carrier gas through the furnace.* A number of carrier gas runs have been made and the population and length of whiskers in the deposition section of the stacked furnace has been greatly improved, although deposition in this large region still provides whiskers of sub-millimeter length. Five hour runs with a temperature of 2100°C in the bottom furnace section and 1600°C in the upper furnace section with a hydrogen flow sufficient to maintain a furnace pressure of 800μ have produced the best results to date. Further improvement is expected through optimization of furnace conditions combined with longer growth period.

c. Chemical Method

The chemical method depends on the production of boron carbide in situ from a gas phase reaction such as:

$$4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HCl$$

A 1" diameter by 8" long ATJ graphite deposition mandrel is placed in the small furnace and varying flows of boron trichloride (Matheson - Technical grade), methane (Matheson-Commercial grade), and hydrogen (Burdett Oxygen Co. - 99.5%), are passed through a furnace at temperatures ranging from 1500-1900°C and at pressures varying from 12 mm down to as low as 18 microns. At the higher pressures and flow rates, anisotropic blades of boron carbide were obtained.

*Under vacuum, the furnace pressure during a run drops from a high of approximately 200μ to a low of approximately 5μ, thus the pressure is too high to provide molecular flow and a maximum rate of vaporization.

Several runs have been made using the dynamic chemical method of gas phase vapor deposition. The feed materials to the stacked furnace were boron trichloride, methane and hydrogen. Flow rates and temperatures have been varied in an attempt to establish the proper growth environment. As yet only poorly characterized whiskers have been observed.

B. MECHANICAL PROPERTIES OF B_4C WHISKERS

The determination of the tensile strength and elastic modulus of B_4C whiskers was initiated in January, 1964. Since then, approximately 17 specimens from eight batches have been tested. All the data to date are shown in Table II.

Testing was performed on a Tecam Micro-Tensile Testing Machine, manufactured by Techne, Ltd., Cambridge, England. The machine, based on a design by D. M. Marsh, has been previously described[11]. Briefly, the machine is of the null-balance type using a torsion balance to apply loads and a mirror autocollimating telescope system to detect extension. Loads between 1 milligram and 400 grams can be applied, and extensions of about 10^{-5} mm can be detected.

Although the tensile machine itself is very accurate, in practice the accuracy of strength and elastic modulus values are limited by two factors; area determination and grip deformation. These limitations are discussed in more detail below.

1. Area Determination

The most direct way to determining the cross-sectional area of a whisker after testing is to retrieve the broken specimen and measure the fracture area directly on a high magnification microscope. This was the primary method used in this investigation. Typical cross-sections are shown in Figures 14 and 15. Triangular cross-sections were observed unambiguously in only two cases; the large majority of whisker cross-sections were parallelograms.

TABLE II. SUMMARY OF B_4C WHISKER TENSILE DATA

Specimen No.	Total Length, mm	Gage Length, mm	Area, μ^2 **	Apparent Elastic Modulus, psi	Ultimate Strength, psi	Cross Section	Whisker-Type (X-ray Diffraction)
60-37-68-1	2.0	0.25	292.0	19×10^6	350,000	Triangle	----------
60-37a-9-5	1.31	0.32	69.7	37×10^6	184,000	"	----------
60-37a-9-6	0.73	0.14	75.5	22×10^6	315,000	"	----------
60-37a-9-7	2.77	0.72	66.4	71×10^6	934,000	Parallelogram	----------
60-37a-918	0.82	0.145	75.5	17×10^6	330,000	"	----------
60-37a-9-9	0.93	0.20	40.6	31×10^6	536,000	"	----------
60-37a-18-10	1.97	0.69	67.5	41×10^6	323,000	"	A
60-37a-18-11	0.55	0.15	12.2	31×10^6	350,000	"	----------
60-37a-18-12	0.67	0.21	7.4	23×10^6	615,000	"	----------
60-37a-25-13	2.27	0.26	542.0	24.5×10^6	401,000	"	A
60-37a-25-14	3.04	1.10	99.3	67.1×10^6	573,000	"	A
60-37a-34-15	5.90	4.23	304.0	61.7×10^6	----	"	----------
60-37a-36-16	4.21	2.05	169.0	76×10^6	179,000	"	----------
60-37a-36-17	2.23	0.97	160.0	47×10^6	----	"	----------
60-37a-39-18*	4.50	1.85	168.0	35×10^6	265,000	"	----------
60-37a-39-19*	4.01	1.60	89.6	66×10^6	865,000	"	----------
60-37a-46-20	4.41	2.85	511.0	34×10^6	207,000	"	----------
60-37a-46-21	----	0.81	4.6	108×10^6	965,000	"	----------
60-37a-46-22	4.43	2.66	48.0	41.4×10^6	142,000	"	----------

* Area determined metallographically.

** $1\mu^2 = 1.55 \times 10^{-9}$ in.^{2}

Figure 14. Fracture Surface of B_4C Specimen No. 1 After Failure - 583X.

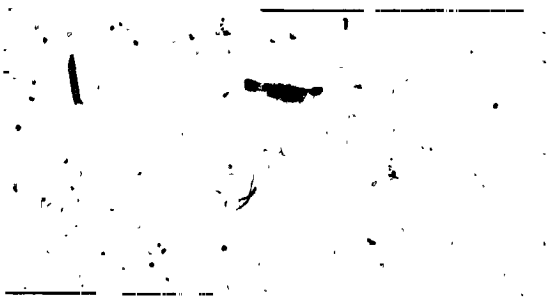


Figure 15. Typical Fracture Face of a Tested B_4C Whisker - 584X.

The normal method of measuring the area after test is to photograph the fracture face at a known high magnification, cut out the fracture area from the photograph and weigh it. The area is calculated by making a comparative weighing of several one inch square specimens cut out from the same photograph. The difficulty comes when the fracture is not perpendicular to the specimen axis. In this case, additional measurements must be made of the specimen by photographing the sides, with the attendant troubles of light reflection and the uncertainty of the location of the major dimensions. It is estimated that an error of about ± 30% is present in the fracture areas determined to date by this method.

Metallographic techniques were investigated to more precisely measure the fracture area. Several specimens were mounted in a cold-setting clear resin, and ground and polished down to slightly past the fractur surface. One such section is shown in Figure 16. In this particular case, the metallographic method gave an area within 3% of the fracture surface valu In another case, a 40% discrepancy was observed. It may be pointed out that the metallographic method may also yield ambiguous results. This comes about because of chipping of the mount near the specimen, which makes it difficult to measure the area. Several additional fractured specimens have been potted and will be examined.

2. Grip Deformation

Although the testing machine is fundamentally capable of producing very accurate force-extension curves for small specimens, its

accuracy is limited in practice by shear deformation of the diphenyl carbazide glue holding the specimen to the anvil. A crude and elementary analysis of this behavior is shown in Appendix A. Using a value of $\frac{E_f^*}{G_p} = 4000$, Figure 17 was constructed. While 5 points are outside of the scatter band, it would seem that equation (1A) in Appendix A is at least qualitatively correct. The points outside the scatter band probably indicate excessively large experimental error, but may represent whiskers of a different orientation and hence of a different elastic modulus.

Another geometric feature of whiskers that may lead to errors in the computed elastic modulus is the taper present in most whiskers. As shown in the Appendix, this effect is not large unless an extremely tapered whisker is tested. These types are rejected upon initial examination with a stereo-microscope.

Strength data obtained to date as a function of area are shown in Figure 18. The scatter observed is partially due to the difficulties associated with the area measurements, as previously discussed. In addition, batch variations and variations of whisker quality within a particular batch are undoubtedly responsible for a considerable portion of the observed experimental scatter. The estimated mean line "through" the data points must be considered extremely tentative. Indeed, little justification except for past work on α-Al_2O_3 whiskers exists for drawing the line with a negative slope.

C. CRYSTAL AND MORPHOLOGICAL CHARACTER OF B_4C WHISKERS

The purposes of this phase of the program have been: (a) to verify that the filamentary crystals (whiskers) which were produced were B_4C; (b) to establish whether they were poly- or single-crystals; (c) to determine their crystal habit or orientation; (d) to investigate their morphological character in terms of their perfection and; (e) to correlate the above findings with controlled variations in production techniques and with the observed tensile strengths of the whiskers tested. It was believed that this approach

* E_p = Elastic modulus of Fiber (psi), G_p = Shear modulus of plastic.

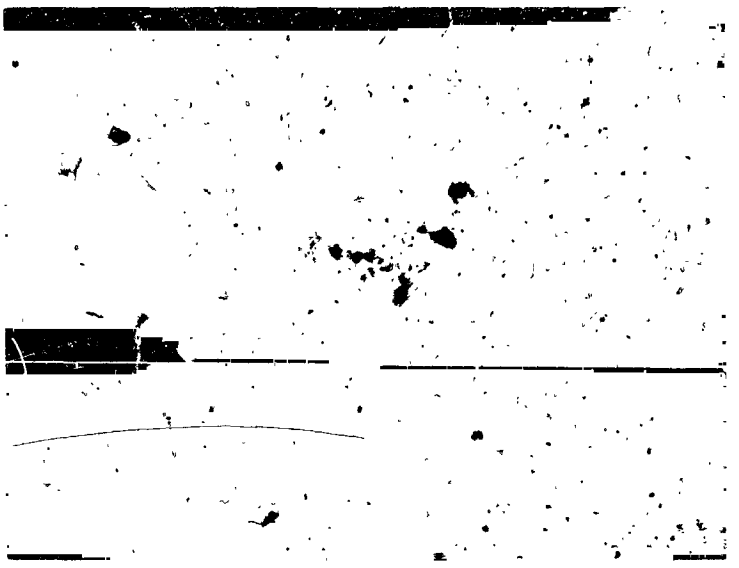


Figure 16. Cross-Section of Mounted and Polished B_4C Whisker - 1210X.

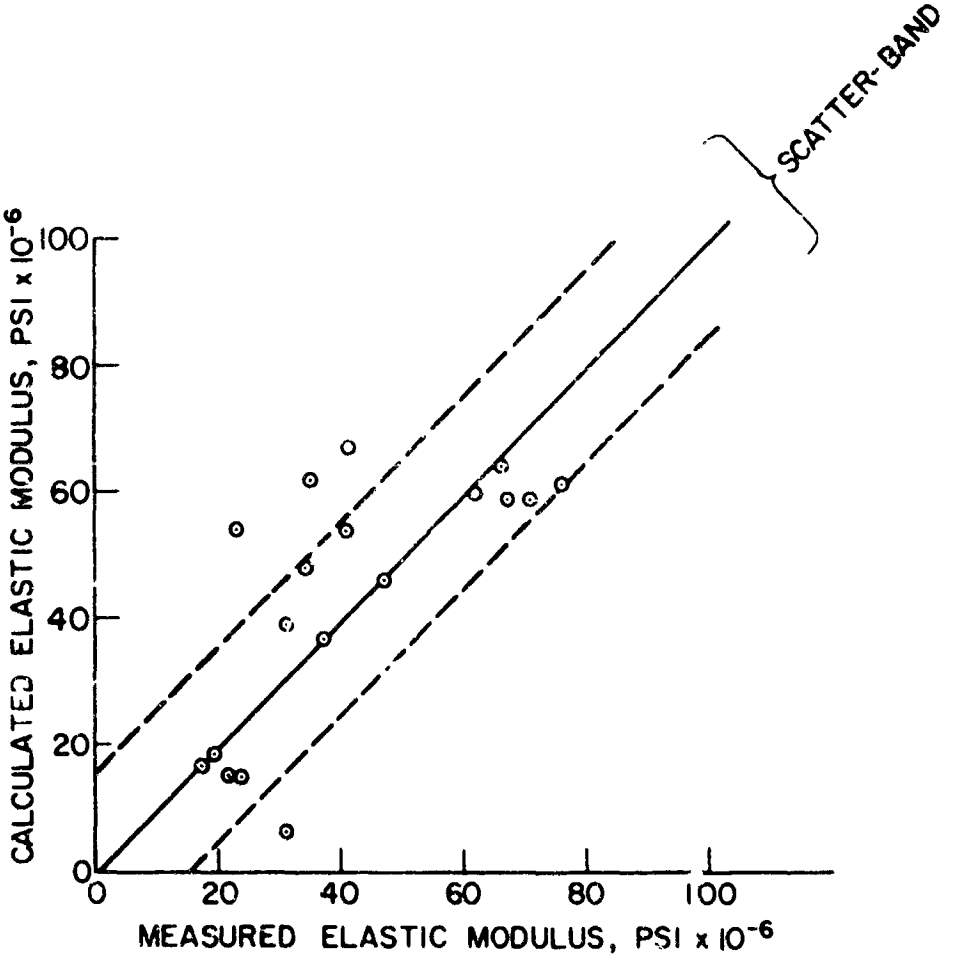


Figure 17. Relation Between Measured and Calculated Elastic Modulus.

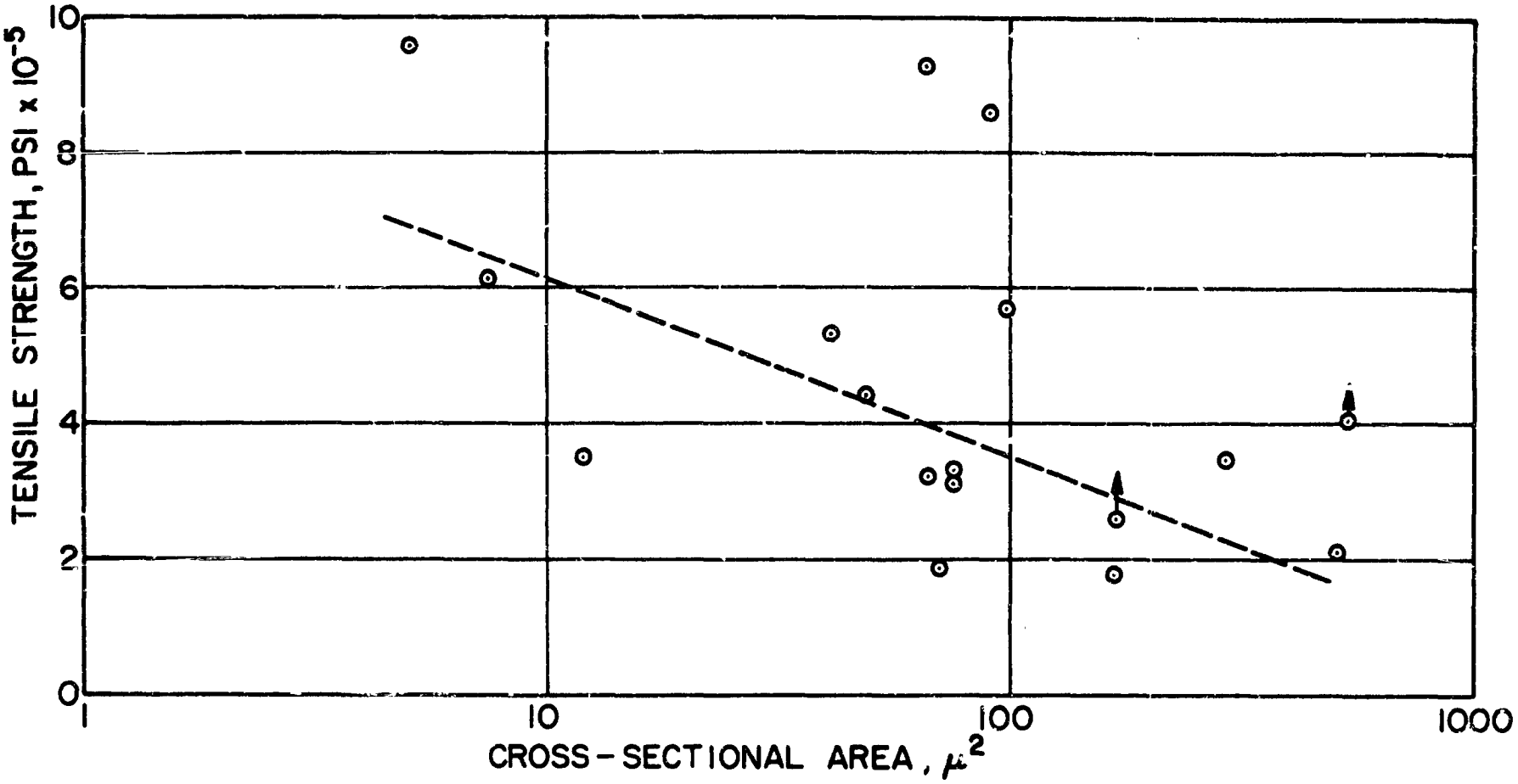


Figure 18. Tensile Strength of B_4C Whiskers as a Function of Area.

would aid in the optimization of process variables in order that strong B_4C whiskers could be produced routinely.

In all but the very first cases, independent of the production run, whether the whiskers were examined individually or ground together to produce a powder, and, then examined, x-ray diffraction confirmed, that the whiskers were single phased B_4C. Only from the earliest pure vapor phase production runs, before the optimization of the process parameters were begun, was there evidence of a second crystalline phase present. The presence of a second phase, on the x-ray diffraction photographs, was manifested in a medium intensity diffraction line not belonging to B_4C and which arose from a reflection from a family of crystalline planes which had an interplanar separation, d, of 3.36Å. Subsequent electron microscopy and electron diffraction investigations revealed that B_4C whiskers from these early production runs were coated with a thin graphite film. And indeed, the 3.36Å interplanar separation is accountable as the (002) spacing of graphite. In Figure 19 is presented a powder x-ray diffraction photograph produced from pulverized B_4C whiskers obtained from a typical early run. The arrow on this photograph indicates the position of the (002) 'reflection' for graphite, the remaining lines in this photograph, have been shown to belong to B_4C.

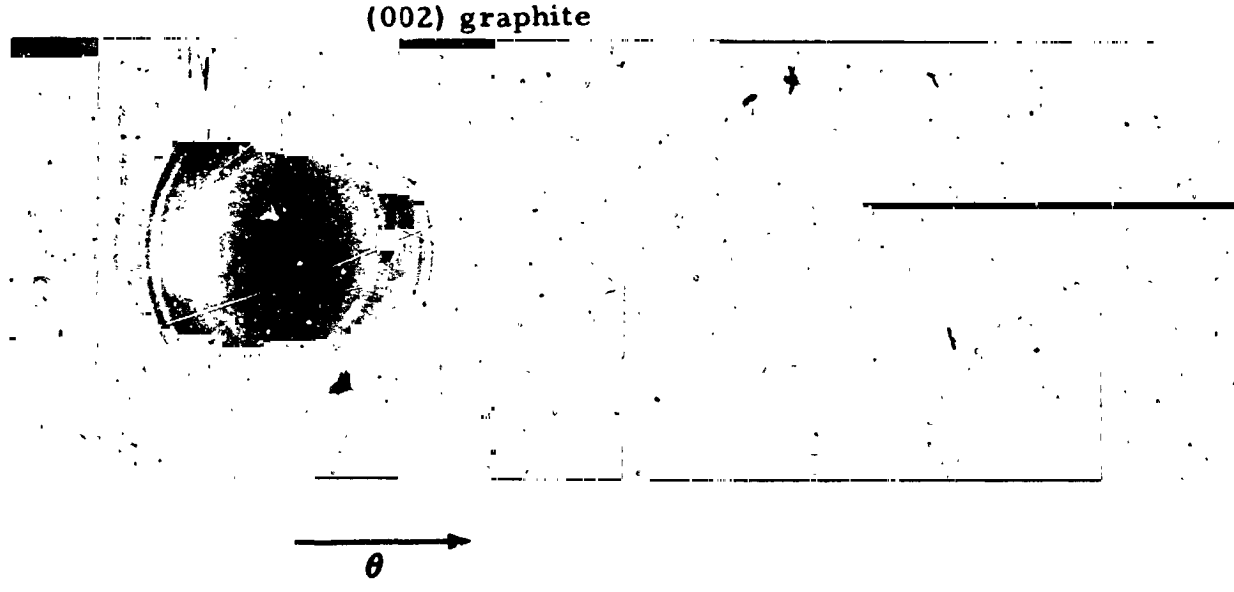


Figure 19. X-Ray Diffraction Photograph From B_4C Whisker Specimens (Cu Radiation, 57.3 mm ϕ Camera).

In Table III are presented the x-ray diffraction data as obtained from the photograph in Figure 19. In this table, the experimental data is compared with the published data[12] on B_4C.

The excellent agreement between the experimental x-ray data and the published or reference data for B_4C indicates that the whiskers are B_4C. The additional medium intensity line (see arrow Figure 19) with d = 3.36Å can be indexed as the (002) reflection for graphite (d_{002} graphite = 3.37Å). The fact that graphite appears to be present is in agreement with the before mentioned electron diffraction observations.

Electron diffraction and x-ray diffraction examination of individual B_4C whiskers, when the whiskers were produced by the methods described in this report, showed that they were single crystal. The single crystal character of these whiskers is evidenced by the nature of the diffraction patterns which they yielded. For example, the regular spotty nature of the selected area electron diffraction photograph of Figure 20-b, produced from the region of a B_4C whisker shown in the transmission electron photomicrograph of Figure 20-a, indicates its single crystal character.

Analysis of rotation, or layer line, x-ray diffraction photographs revealed the following facts about the B_4C whiskers* which were obtained from the earliest production runs: (a) since the diffraction spots were not sharp, that the whiskers possessed imperfections and; (b) that the characteristic repetition distance along the principal growth direction was 5.2Å. The literature[12] indicates that B_4C has an hexagonal structure with the following unit cell dimensions: a_o = 5.61Å and c_o = 12.07Å. Therefore, since the characteristic repetition distance along the major whisker axis was found to be 5.2Å, the major axis was obviously not parallel to either the 'a' or the 'c' hexagonal crystallographic directions. If the Miller indices (hkℓ), where h, k, ℓ are based on a hexagonal unit cell, obey the rule: 1/3 (-h + k + ℓ) = an integer, then a rhombohedral unit cell may be used to describe the structure.

*Note: The 'average' whisker size from the early runs was about 0.7 mm long with a cross section of about 0.01 mm x 0.04 mm.

TABLE III

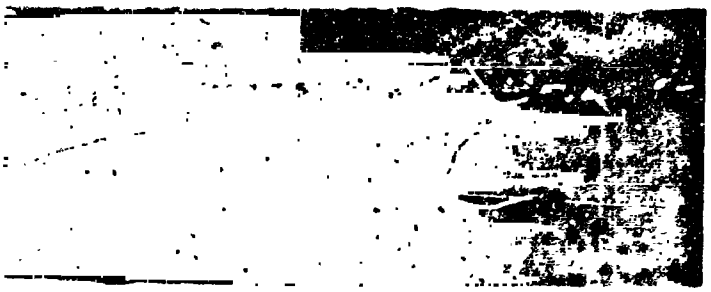
X-RAY DIFFRACTION DATA FROM

BORON CARBIDE WHISKERS

COMPARED WITH STANDARD DATA FOR B_4C

From Diffraction Photograph from Figure 19		From ASTM Card for B_4C (Card 6-0555)		
I	d(Å)	I	d(Å)	(hkl)
m	4.47	30	4.49	101
ms	4.05	40	4.02	003
s	3.78	70	3.79	012
ms	3.36	--	---	---
vvw	3.20	--	---	---
w	2.80	30	2.81	110
vvw	2.61	--	---	---
vs	2.57	80	2.57	104
vvs	2.38	100	2.38	021
vvw	2.31	10	2.30	113
m	2.08	10	2.02	006
vvw	1.81	10	1.82	211
mw	1.71	30	1.714	205
--	---	10	1.637	116
--	---	10	1.628	107
mw	1.50	20	1.505	303
m	1.46	30	1.463	125
m	1.44	30	1.446	018
ms	1.40	30	1.407	027
vw	1.36	20	1.345	009
w	1.33	20	1.342	131
w	1.31	20	1.326	223
vw	1.28	10	1.286	208
w	1.26	20	1.261	306
w	1.19	10	1.191	042

I = relative intensity; w = weak, m = medium, s = strong, v = very
Note: B_4C is hexagonal, a_o = 5.61A, c_o = 12.07A



(a)

Magnification 11,000 X

(b)

Figure 20. Transmission Electron Photomicrograph of a Typical B_4C Whisker (a) and an Electron Diffraction Pattern of the same Whisker (b)

This is the case for B_4C. Wyckoff[13] offers the following rhombohedral unit cell parameters for B_4C, $a_o = 5.19\text{Å}$ and $\alpha = 66^\circ 18'$. Hence, the principal whisker axis, for which the repetition distance is 5.2Å, is parallel to a rhombohedral unit cell edge. Considering the vector repetition distance, $\bar{p} = u\bar{a}_1 + v\bar{a}_2 + w\bar{c}_3$, where a_1, a_2 and c are the hexagonal unit cell edge lengths it can then be shown that any diffraction spot on a layer line diffraction photograph must obey the relationship: $uh + vk + wl = m$, where m = the layer line number (m = 0, for the equator line). Indexing the layer line photographs then showed that these B_4C whiskers had their long axes parallel to either the 1/3 $(-\bar{a}_1, \bar{a}_2 + \bar{c})$ and/or the 1/3 $(-\bar{a}_1 - 2\bar{a}_2 + \bar{c})$, rhombohedral unit cell edges. The above analysis concerns only those B_4C whiskers which were obtained from early production runs.

During later production of B_4C whiskers, through refinements in the growth procedure, longer whiskers (c.a. 2mm and longer) were made available for study. X-ray diffraction again revealed that these longer whisker were single phase B_4C and single crystal fibers. However, unlike the early whiskers in which the major whisker axis was found to be parallel to a rhombohedral cell edge, the later whiskers were <u>all</u> found to have their major axis oriented parallel to the 'a' hexagonal cell edge, i.e., parallel to the ⟨100⟩ crystallographic direction.

In Figure 21 is shown an enlarged (2.2X) portion of an indexed 'layer line' x-ray diffraction photograph which was produced from a typical B_4C whisker obtained after optimization of the growth process. The well defined spots indicate the single crystal character of the specimen. From measurements made on the separation distances of the 'layer-lines', y_1, and y_2, on the original diffraction photograph, and from a knowledge of the wavelength, λ, ($\lambda = 1.5405\text{Å}$ for $CuK\alpha_1$, radiation) and radius, R, of the cylindrical diffraction camera, the repetition distance, p, along the axis of the fiber (crystal rotation axis) was obtained from the easily derived relationship:

$$p = m\lambda \left(1 + R^2/y_m^2\right)^{1/2},$$

where m = the layer line number, m = 0, 1, 2, 3.....

Figure 21. X-ray Diffraction Photograph (2.2X) of a Typical "a" Type B_4C Whisker.

It was thus determined that the repetition distance in all the long whiskers examined was 5.60Å ± 0.02Å. This distance compares very favorably with the literature[12] value for the length of the a-crystallographic edge of the hexagonal unit cell of B_4C, a_o = 5.61Å. Hence for these whiskers the major whisker axis was parallel to the a-crystallographic direction, ⟨100⟩. Because of alignment problems in the x-ray apparatus due to the small dimensions of the whisker cross sections, the external faces of the B_4C whiskers have not yet been positively identified. However by making inferences from the morphological character of typical overgrowth structures on whisker surfaces, from optical and electron photomicrographs, and from the knowledge that the major growth axis is parallel to the 'a' crystallographic

direction, one is led to believe that one pair of whisker faces are probably of the (00ℓ) type while the two others are probably of the (0kℓ) type. In Figure 22 is shown a schematic representation of the types of overgrowth which have been observed on the surfaces of 'a' type whiskers. The (00ℓ) face is labeled as is the (0k0) face. Both $\bar{a}_1$ and $\bar{a}_2$ of the hexagonal unit cell are parallel to the face of the whisker on which the overgrowths are shown, the (00ℓ) face. Since the $\bar{a}_1$ direction is parallel to the major axis of the whisker then the plane normal to the major axis is a (2n, n, 0) plane, where n = ± 1, 2, 3....., this plane is also indicated in Figure 22.

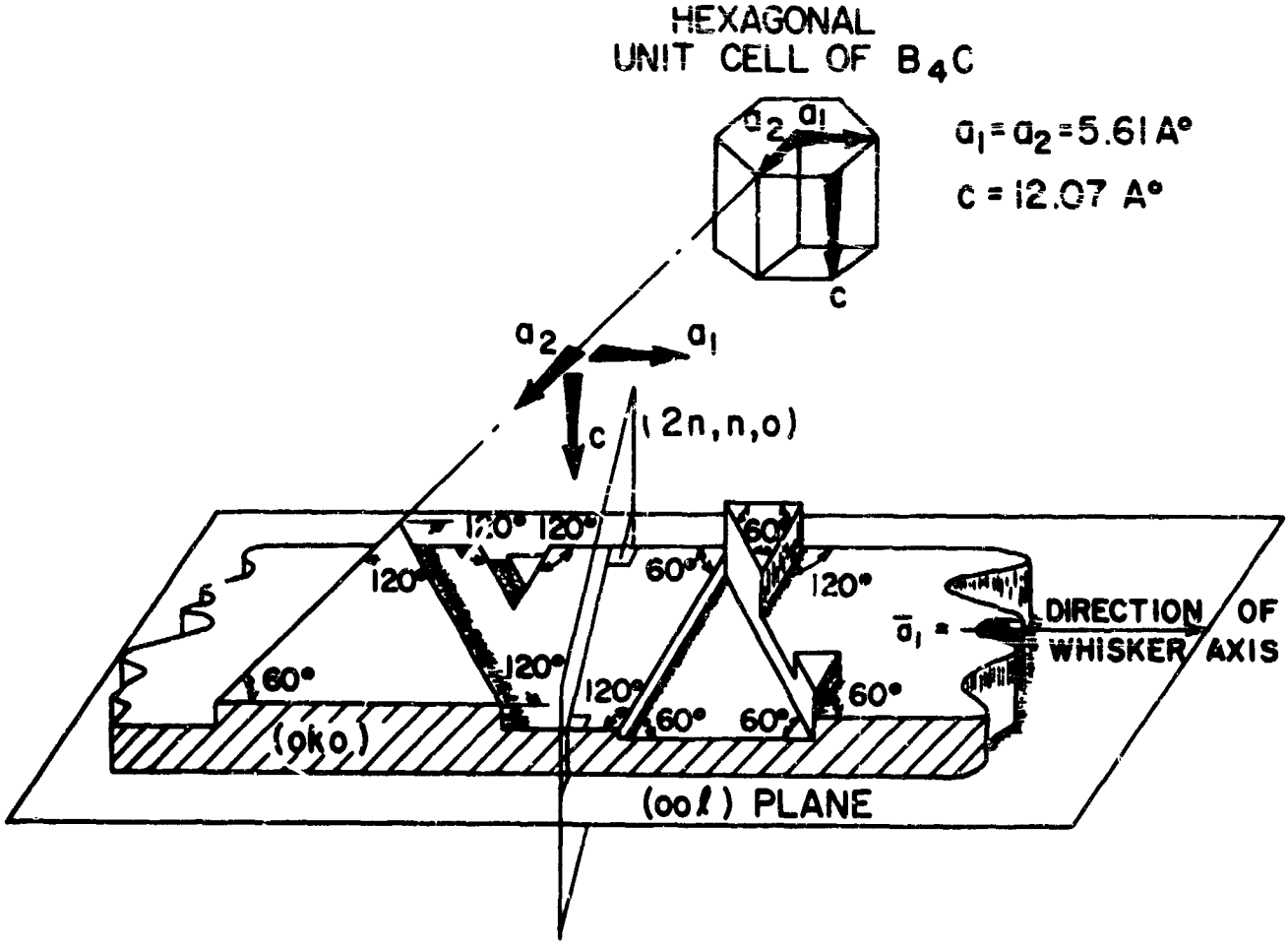


Figure 22. Schematic Representation of Typical Overgrowths Observed on B_4C Whiskers. (Also Refer to Figure 11).

Results of Crystal and Morphological Characterization of B_4C Whiskers.

(a) Every whisker examined by x-ray diffraction methods, independent of the production run from which the whiskers were randomly chosen for examination, proved to be B_4C. Only from the earliest production runs, before optimization of process parameters, was a second crystalline phase, graphite, detected.

(b) B_4C whiskers grown from the pure vapor phase are generally single crystal.

(c) In all later runs, after optimization of process variables, the resulting long whiskers (c.a. 2mm and longer) were found to have their major axes parallel to the $\bar{a}$ crystallographic direction* (based on an hexagonal unit cell). The short (c.a. 0.7mm in length) whiskers obtained from the earliest production runs were found to have their major axes parallel to the rhombohedral unit cell edges, $1/3\ (-\bar{a}_1 + \bar{a}_2 + \bar{c})$ and/or $1/3\ (-\bar{a}_1 - 2\bar{a}_2 + \bar{c})$.

(d) The whiskers were observed to have surface overgrowth structures*. This anomalous structure was found to be severe in weak crystals and very mild in strong ones.

Experimental procedures which were found useful in the x-ray and electron microscopy investigations of B_4C whiskers are described in the Appendix of this report.

D. COMPOSITE STUDIES

It has been shown by Jech and Weeton[14] that short fibers can strengthen a relatively weak material through the mechanism of stress transfer from fiber to fiber through the matrix. The important variables in composite theory then are ideally the strength of the fiber itself, the volume fraction of fiber in the composite and the length-to-diameter ratio

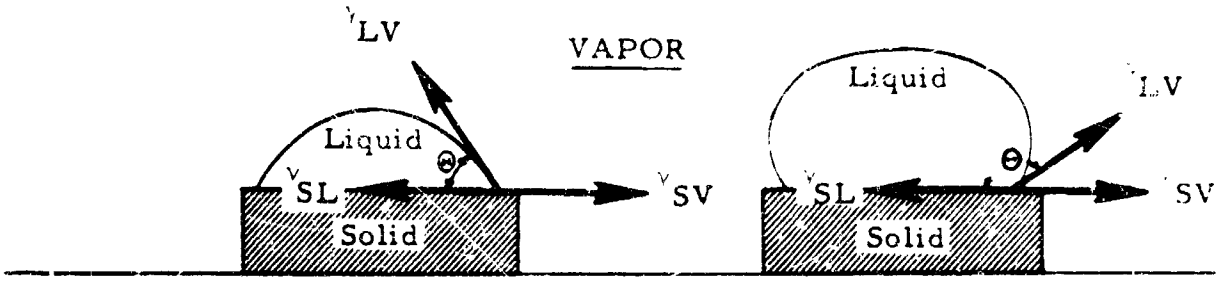
*Note: Although the small cross sectional size of the availabl. whiskers ($5\mu^2$ to $500\mu^2$) precluded positive x-ray identification of the well formed external crystal faces, the form of the overgrowth structure on these faces along with a knowledge that the whiskers were of the 'a' type, enabled an inference to be made that one pair of external crystal faces was possibly of the (00ℓ) type. (The (00ℓ) plane is parallel to the basal plane of the hexagonal unit cell of B_4C). On the basis of this inference, four possible quadrilateral cross sections were postulated.

of the fiber. Of major importance aside from strength and geometric factors is the nature of the interface between the fiber and its surroundings. Without proper bonding (wetting) there can be no transfer of stress from fiber to fiber. Accordingly, initial wetting experiments for a choice of metal matrix materials for composites have been directed toward the study of the wetting of bulk B_4C by the following metals: Fernico 5, nickel, gold, silver and copper. The wetting ability of liquids on solids can be described by the contact angle θ illustrated in Figure 25. Wetting can thus proceed from no wetting (90° contact angle) to complete wetting (0° contact angle). The results of these studies are shown in Table IV and Figures 26 and 27. Figure 26 shows the wetting of the above metals (from left to right in that order) in hydrogen atmosphere heated at the temperatures and times tabulated in Table IV. Figure 27 of sessile drops of nickel, copper and Fernico 5 shows a more sophisticated approach utilizing a sessile drop apparatus described elsewhere by Sutton[15]. The wetting angle of 30° for Fernico 5 in vacuum is indicative of good wetting. Future metal-B_4C composite work will utilize Fernico 5 matrix as an initial choice.

Studies of epoxy by composites were also initiated. The fabrication of resin based composites do not present as complicated a problem when compared to metal based composites, since wetting is excellent and processing temperatures are not high. Composites were made utilizing PJ-122*[17] epoxy resin and various B_4C whisker batches as designated in Table V. The technique is essentially that developed by Jakas[16] for forming Al_2O_3 whisker-epoxy composites. The B_4C whiskers are packed into glass capillary tubes and then infiltrated with the epoxy. An as-filtered sample of B_4C whiskers, still in its glass capillary tube is shown in Figure 28. Specimens fabricated in this manner have approximate diameters varying between .01 and .02 inches. The packed infiltrated capillaries were then cured by heat at $180^\circ F$ for about 16 hours. The glass sheath was next removed by dissolving

*PJ-122 - a resorcinol diglycidyl ether containing methylnadic anhydride, an EM 207 plasticizer, and a benzyldimethyl amine catalyst.

A. SOLID, LIQUID AND VAPOR UNDER EQUILIBRIUM CONDITIONS



(1) WETTING, $\theta < 90^{\circ}$ (2) NON-WETTING, $\theta > 90^{\circ}$

B. SYMBOLS

γ = surface energy (ergs/cm^2)
for liquids; surface tension (dynes/cm)

Subscripts

S, L, V = solid, liquid, vapor

θ = contact angle between solid-liquid and liquid-vapor interfaces

S = spreading coefficient; if S is positive, liquid will spread over solid surface

W = work of adhesion; the energy required to separate the liquid and solid at the interface

C. RELATIONSHIPS

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta \quad (1)$$

$$S_{SL} = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \quad (2)$$

for spreading: $\gamma_{SV} > \gamma_{LV} + \gamma_{SL}$ (3)

$$W = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (4)$$

or $$W = \gamma_{LV} (1 + \cos \theta) \quad (5)$$

Figure 25. Surface Energy Relationship Between Solid, Liquid and Vapor Interfaces from Sutton.

TABLE IV. SUMMARY OF WETTING EXPERIMENTS WITH B_4C AND VARIOUS METALS IN HYDROGEN ATMOSPHERE AND VACUUM

Metal	Temp.	Time	Contact Angle H_2	Contact Angle Vacuum
Silver	1100°C	1 hr.	$\theta > 90^\circ$	--
Copper	1100°C	1 hr.	$\theta > 90^\circ$	$>90^\circ$
Gold	1100°C	1 hr.	$\theta > 90^\circ$	--
Nickel	1500°C	1 hr.	$\theta < 90^\circ$	80°
Fernico "5"	1500°C	1 hr.	$\theta < 90^\circ$	80°

in HF. No reaction of the epoxy with HF was noted. The B_4C reinforced epoxy specimens were fitted with epoxy grips and then tested in an Instron tensile tester with a chart speed of 2"/min and a cross head speed of .02/min. A typical specimen before testing is shown in Figure 29. A special testing jig, Figure 30, has been developed previously[16]. It has been designed to keep specimens as aligned as possible in order to minimize specimen bending which could exaggerate grip failure. The epoxy knobs are slipped into mating grip depressions and the load applied.

Table V is a compilation of tensile data derived from four micro-composites. As specimens were loaded and broken new grips were applied until the specimen became too short to test. Many tests are obviously premature grip failures or gross defects in the specimens. Condition of the tests are recorded in the remarks column.

Specimen diameter was measured by averaging many readings through a filar eyepiece at 40X. Representative specimens were mounted in epoxy mounts, polished and photographed at 200X in order to determine the volume fraction of B_4C whiskers contained in the micro-composites with volume fraction data determined by a point count method. Each composite contained approximately 10% by volume B_4C whiskers. Figure 31 shows a cross-section at 200X of a typical epoxy-B_4C composite.

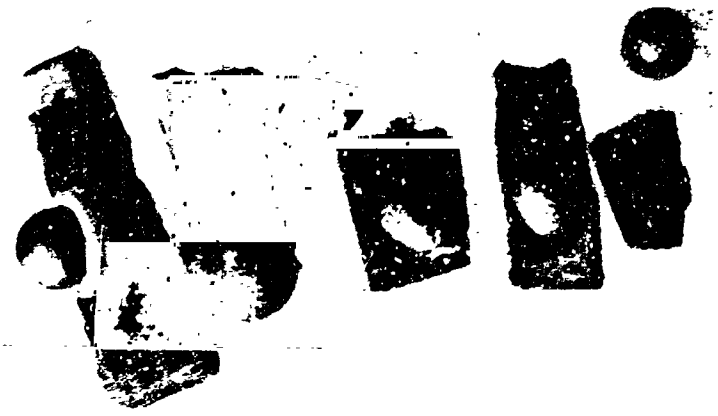


Figure 26. The Wetting of B_4C by the Metals (From Left to Right) Fernico 5, Nickel, Gold, Silver and Copper in Hydrogen -3X.

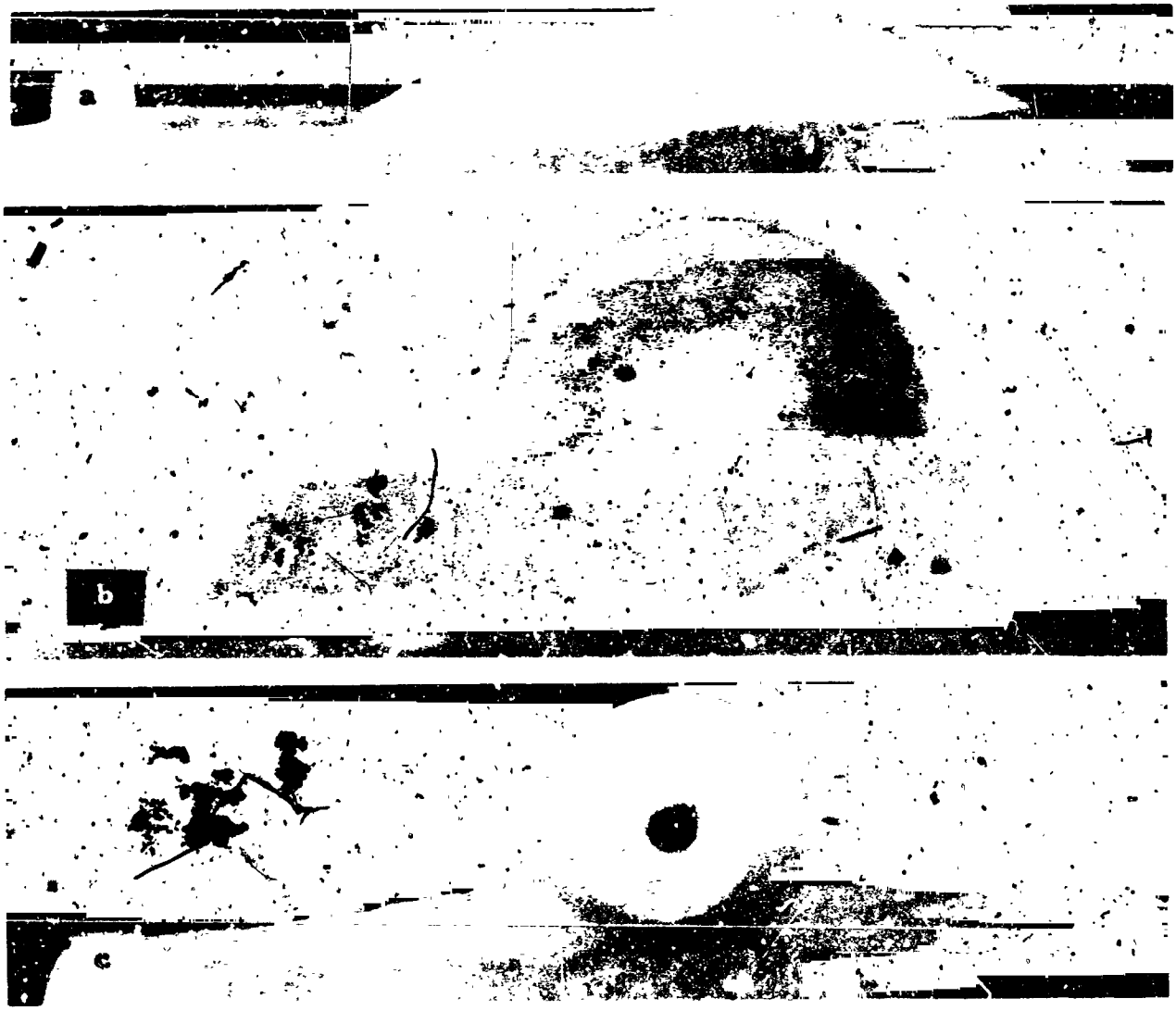


Figure 27. Sessile Drops of
a. Copper
b. Nickel
c. Fernico 5"
on Bulk B_4C in Vacuum - 15X.

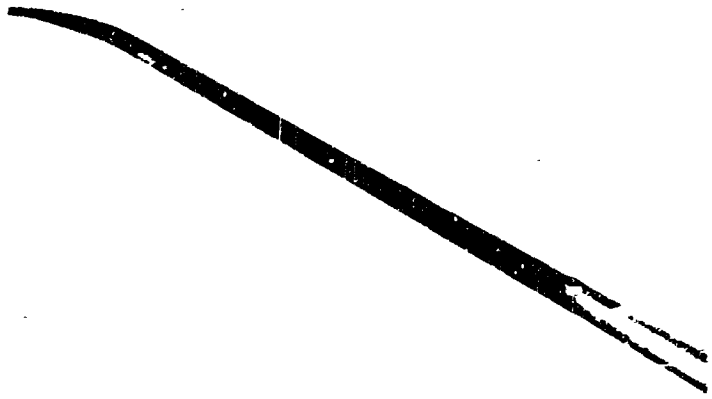


Figure 28. Whiskers Infiltrated with PJ 122 Epoxy. Still in Glass Capillary Tube.

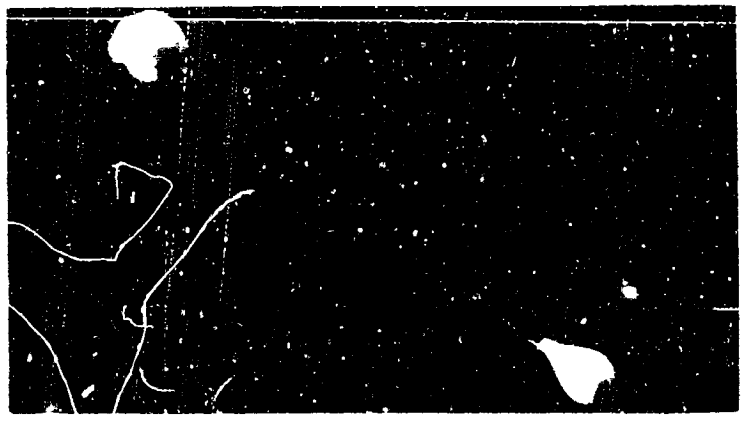


Figure 29. Typical B_4C Epoxy Composite Tensile Specimens.

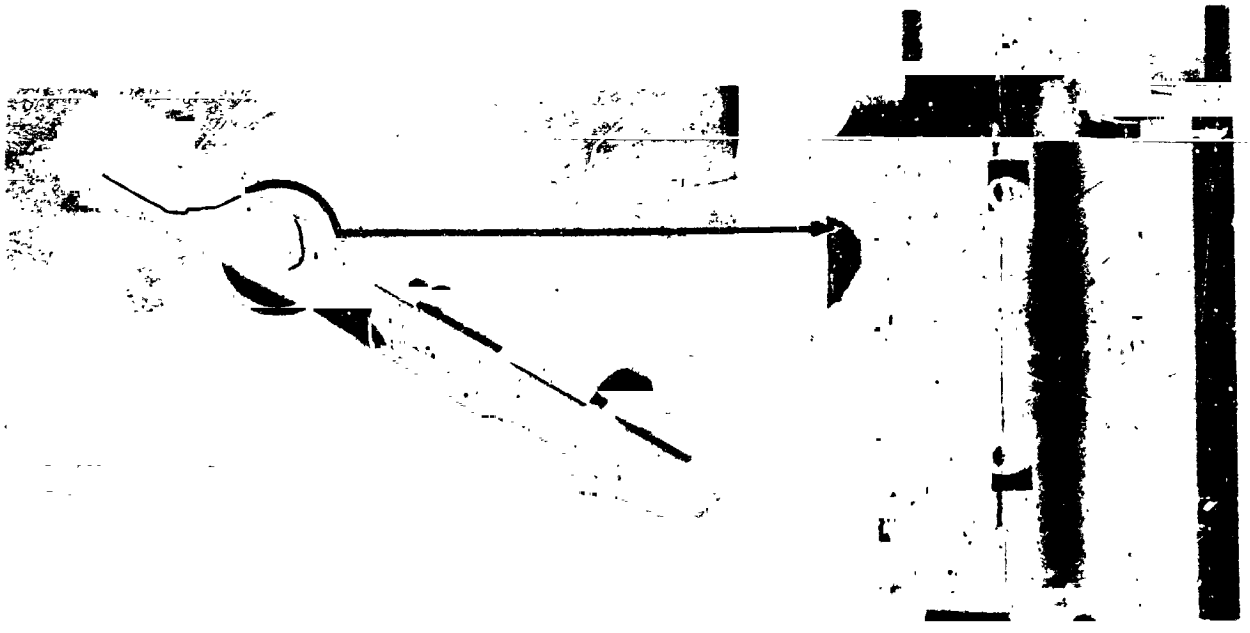


Figure 30. Tensile Testing Jig (about 1/4 actual size).

TABLE V. TENSILE DATA OF B_4C-REINFORCED PLASTIC SPECIMENS

Run No.	Breaking Load(lbs)	σ_c* (Breaking stress) psi	$\bar{\sigma}_c$* (psi) (B_4C)	Remarks
60-37a-57-1	5.45	11,600	62,000	Broke in grip
-2	---			Broke on loading
-3	3.25	6,900	15,000	Broke in grip
-4	4.95	7,450	20,500	Broke in grip
-5	4.9	9,850	44,500	Broke in grip
-6	7.05	14,200	88,000	Broke in grip
60-37a-43-1	2.40	14,200	88,000	Broke in grip
-2	---			Broke on loading
-3	1.4	5,190	---	Obvious defect (void)
-4	4.95	20,000	146,000	Broke in grip
-5	4.98	16,800	114,000	Broke in grip
-6	.675	4,075	---	Obvious defect (void)
-7	4.1	24,700	193,000	Broke in grip
60-372-47-1	1.40	4,025	---	Obvious defect (tweezer damage)
-2	3.275	9,450	40,500	Broke in grip
-3	3.32	6,680	12,800	Broke in grip
-4	6.2	10,200	48,000	Broke in grip
60-37a-57/35-1	1.25	7,500	21,000	Broke in grip
-2	---			Broke on loading

*σ_c, σ_f = Strength of composite and fibers respectively. (Composite contains approximately 10% whiskers)

Note: All whiskers utilized in above composites were shorter than all test gauge lengths.

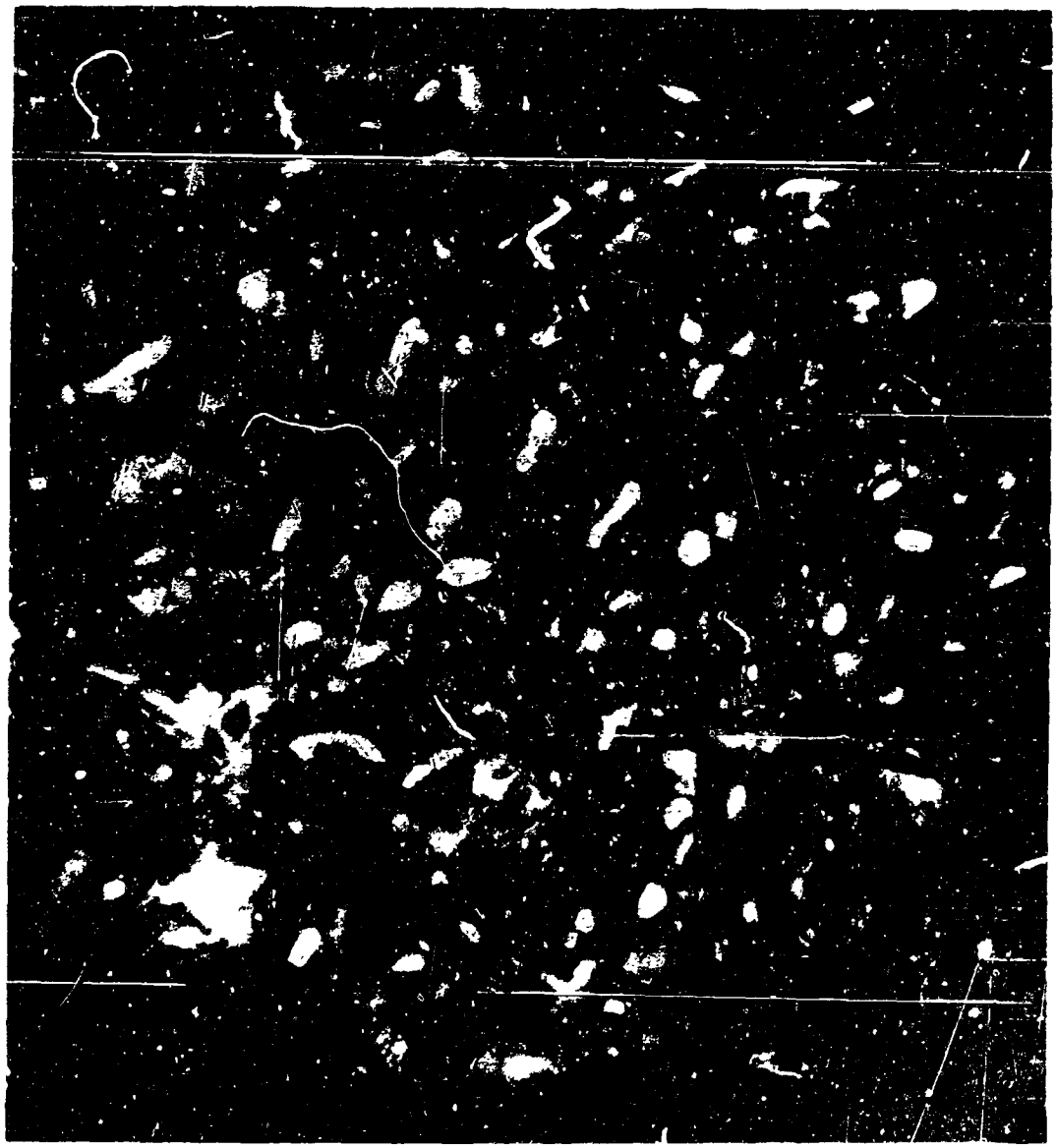


Figure 31. Cross-Section of Typical Epoxy-B_4C Composite (200X).

Specimens of PJ 122 epoxy were also made as a control. These specimens were also tested in tension and an average value of 6000 psi was measured for this particular batch. (A value of σ_m = 6000 psi was thus used in subsequent calculations for determining the average stress in the B_4C whiskers, σ_f)

The effective strengthening parameter σ_c, was calculated by utilizing a law of mixture relationship developed by Jech and Weeton[14] which states that the total strength of the composite σ_c is a combination of the matrix strength (σ_m) times its volume fraction plus the whisker stregth (σ_t) times its volume fraction ($\sigma_c = \sigma_m F_{vm} + \sigma_f F_{rf}$). It can also be seen from this relationship that the strength due to fibers in a composite is primarily dependent on the strength and volume fraction of the whisker phase, and is independent of the matrix material, provided that the matrix can support a shear stress equivalent to the tensile load on the fiber and that the matrix is able to transfer the tensile load from fiber to fiber. An example of the low shear stresses involved can be derived from the work of Sutton[16] et al on silver-Al_2O_3 whisker composites where reinforced silver was stressed to 82,000 psi at 1600°F, silver at those temperatures has an intrinsic tensile strength of near 1,000 psi. The highest average stress supported by B_4C whiskers occurred in test No. 60-37a-43-7 and was calculated to be 193,000 psi. Thus far all whiskers grown during a run were used in a resulting composite with no attempt made to select whiskers according to any criteria which could maximize results, i.e., favorable l/d ratio, small diameter, smooth crystals without obvious overgrowth, etc. Therefore the average strengths measured thus far are not indicative of what is to be expected in future work. These initial attempts are primarily designed to learn techniques which can be used to produce small testable composites, with further work oriented toward maximizing strengthening by using a more judicial choice of whiskers.

IV. CONCLUSIONS

1. Boron carbide B_4C, whiskers have successfully been produced, which is the first synthesis of this material to be reported in whiskers form.

2. Continued improvedment in the growth of B_4C whiskers has been accomplished. The average length of the whiskers has been steadily increased throughout the contract period so that now whiskers as long as 2 cm have been grown.

3. Utilizing a batch process, whiskers of satisfactory quality and quantity can be grown routinely.

4. Thus far, of the various growth methods tried, the technique of vaporization and subsequent condensation of bulk B_4C has been the best means of producing whiskers of useable size and length.

5. The successful growth of significant quantities of B_4C whiskers of adequate length has enabled the mechanical properties phase of the program to advance steadily. The Young's modulus of B_4C has been determined as approximately 65×10^6 psi.

6. Many of the whiskers are tapered. The significance of the taper on the measured strength of the whisker was assessed theoretically.

7. A theoretical study was made of an apparent modulus change as a function of tensile specimen length. Limitations on the testing of micro-samples were defined.

8. Material characterization studies has kept pace with growth and mechanical properties studies. Growth habits have been determined, surface studies of individual whiskers have been made and the equilibrium shapes of whisker cross-sections have been hypothesized.

9. Wetting experiments in hydrogen and vacuum have shown that 'Fernico 5' to be a promising metal matrix material for B_4C - metal composite studies.

10. Preliminary experiments with epoxy-based composites has shown that some strengthening has taken place, and that 10% whiskers has resulted in strengths which are from times that of the unreinforced epoxy. Average stresses up to 193,000 psi have been calculated as being supported by the B_4C whiskers in the composite specimens.

ACKNOWLEDGEMENTS

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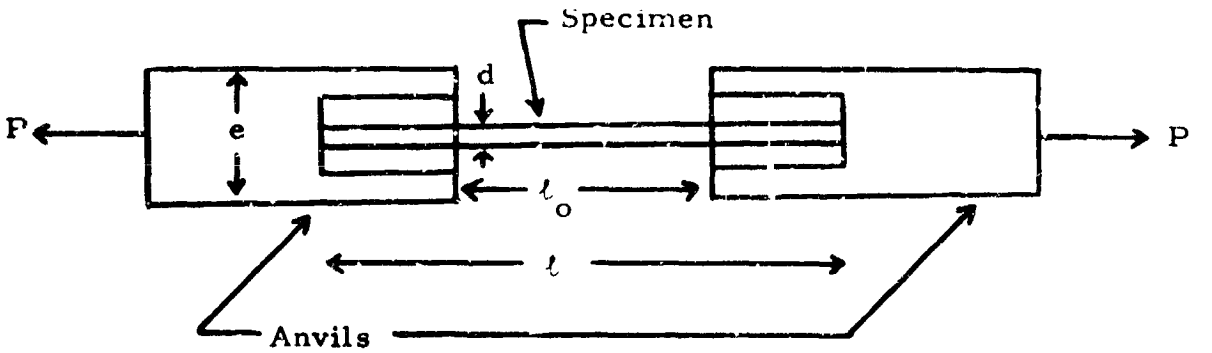
APPENDIX A

EFFECT OF GRIP DEFORMATION ON MEASURED MODULUS



Consider a specimen glued in place on the flat specimen anvils subjected to a load P. The average shear stress in the plastic is given by

$$\tau = \frac{P}{(\ell - \ell_o)(e-d)}$$

Here e is some unknown distance in the plastic throughout which a shear stress exists.

The average shear strain is

$$\gamma = \frac{\Delta}{e-d}$$

Substituting into the linear relation $\tau = G_P \gamma$, we have

$$\frac{P}{(\ell - \ell_o)(e-d)} = G_P \frac{\Delta}{e-d}$$

where G_P = shear modulus of plastic

Then the deflection in the plastic will be

$$\Delta = \frac{P}{(\ell - \ell_o) G_P}$$

The total specimen deflection is given by

$$\delta_T = \frac{P\ell_o}{AE_F} + \frac{P}{(\ell - \ell_o)G_P}$$

where E_F = Young's modulus of fiber

The apparent measured modulus E_F^*, is

$$E_F^* = \frac{P\ell_o}{A\,\delta_T}$$

$$= \frac{P\ell_o}{A\left[\frac{P\ell_o}{A\delta_T} + \frac{P}{(\ell - \ell_o)}\ G_P\right]}$$

Then

$$E_F^* = E_F \frac{1}{1 + \frac{AE_F}{(\ell - \ell_o)\ell_o G_P}}$$

We note that if the shear modulus of the plastic is infinite (no deformation), $E_F^* = E_F$.

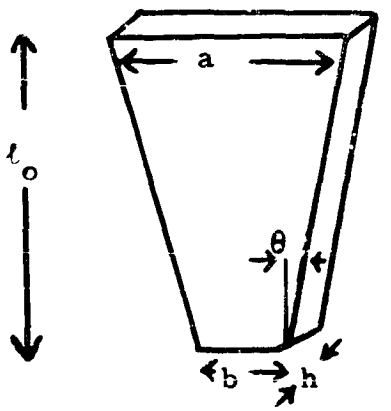
We do not know the shear modulus of the plastic. Furthermore, equation (1A) is inexact because it does not account for the peaking of shear stresses at the free ends. Consequently, the constant $\frac{E_F}{G_P}$ was chosen to best fit the data. The modulus E was assumed to be 70×10^6 psi.

APPENDIX B

EFFECT OF WHISKER TAPER ON APPARENT ELASTIC MODULUS

CASE I. WHISKER TAPERED IN WIDTH DIMENSION ONLY

Consider a whisker with the following free (unbonded) geometry



The deflection of the whisker under a load is given by

$$\delta = \frac{P}{2Eh\,\mathrm{Tan}\theta} \int_{\frac{a-2\ell_o\,\mathrm{Tan}\theta}{2\,\mathrm{Tan}\theta}}^{\frac{a}{2\,\mathrm{Tan}\theta}} \frac{dy}{y}$$

Integrating, we find

$$\delta = \frac{P}{2Eh\,\mathrm{Tan}\theta} \ln \frac{a}{a-2\ell_o\,\mathrm{Tan}\theta} \qquad (1B)$$

For $\theta = 0$, this expression should reduce to the standard elementary equation

$$\delta = \frac{P\ell}{AE}$$

However, for $\theta = 0$, δ becomes indeterminate.

To find the limit, we apply L'Hospital's Rule.

$$\lim_{\theta \to 0} \frac{P}{2Eh} \frac{\ln \frac{a}{a-2\ell_o \mathrm{Tan}\theta}}{\mathrm{Tan}\theta} = \lim_{\theta \to 0} \frac{P}{2Eh} \frac{2\ell_o}{a-2\ell_o \mathrm{Tan}\theta}$$

Therefore, in the limit,

$$\delta = \frac{P\ell_o}{ahE}$$

which is the elementary equation.

CASE II. WHISKER TAPERED IN BOTH WIDTH AND THICKNESS

We assume we have a whisker in the shape of frustrum of a prism and a cross-section of a parallelogram. The taper angle θ is the same. Then

$$\delta = \frac{P}{E} \frac{a}{4h\,\mathrm{Tan}^2\theta} \int_{\frac{a-2\ell_o \mathrm{Tan}\theta}{2\mathrm{Tan}\theta}}^{\frac{a}{2\mathrm{Tan}\theta}} \frac{dy}{y^2}$$

Integrating

$$\delta = \frac{Pa\ell_o}{Eh} \frac{1}{a^2-2a\ell_o \mathrm{Tan}\theta} \qquad (2B)$$

For $\theta = 0$, this expression reduces to the elementary equation

$$\delta = \frac{P\ell_o}{ahE}$$

For both Case I and II, we can find the ratio $\frac{E^*}{E}$ (apparent to actual modulus). The value will depend upon where the area is evaluated.

A. AREA EVALUATED AT MID-POINT

Case I.

$$\frac{E^*}{E} = \frac{2\ell_o \, \mathrm{Tan}\theta}{(a-\ell_o \, \mathrm{Tan}\theta) \, \ln \frac{a}{a-2\ell_o \mathrm{Tan}\theta}}$$

Case II.

$$\frac{E^*}{E} = \frac{a^2 - 2a\ell_o \, \mathrm{Tan}\theta}{(a-\ell_o \, \mathrm{Tan}\theta)^2}$$

B. AREA EVALUATED AT MAXIMUM VALUE

Case II.

$$\frac{E^*}{E} = \frac{a}{a-2\ell_o \, \mathrm{Tan}\theta}$$

C. AREA EVALUATED AT MINIMUM VALUE

Case II.

$$\frac{E^*}{E} = \frac{a-2\ell_o \, \mathrm{Tan}\theta}{a}$$

A plot of $\frac{E^*}{E}$ vs a/b is shown in Figure B-1 for a whisker of the following typical dimensions

ℓ_o = 0.059"

a = 4.13×10^{-4}"

b = 3.31×10^{-4}"

For this figure, it may be concluded that moderately tapered whiskers ($\frac{a}{b} < 1.25$) do not change the measured elastic modulus by a large amount.

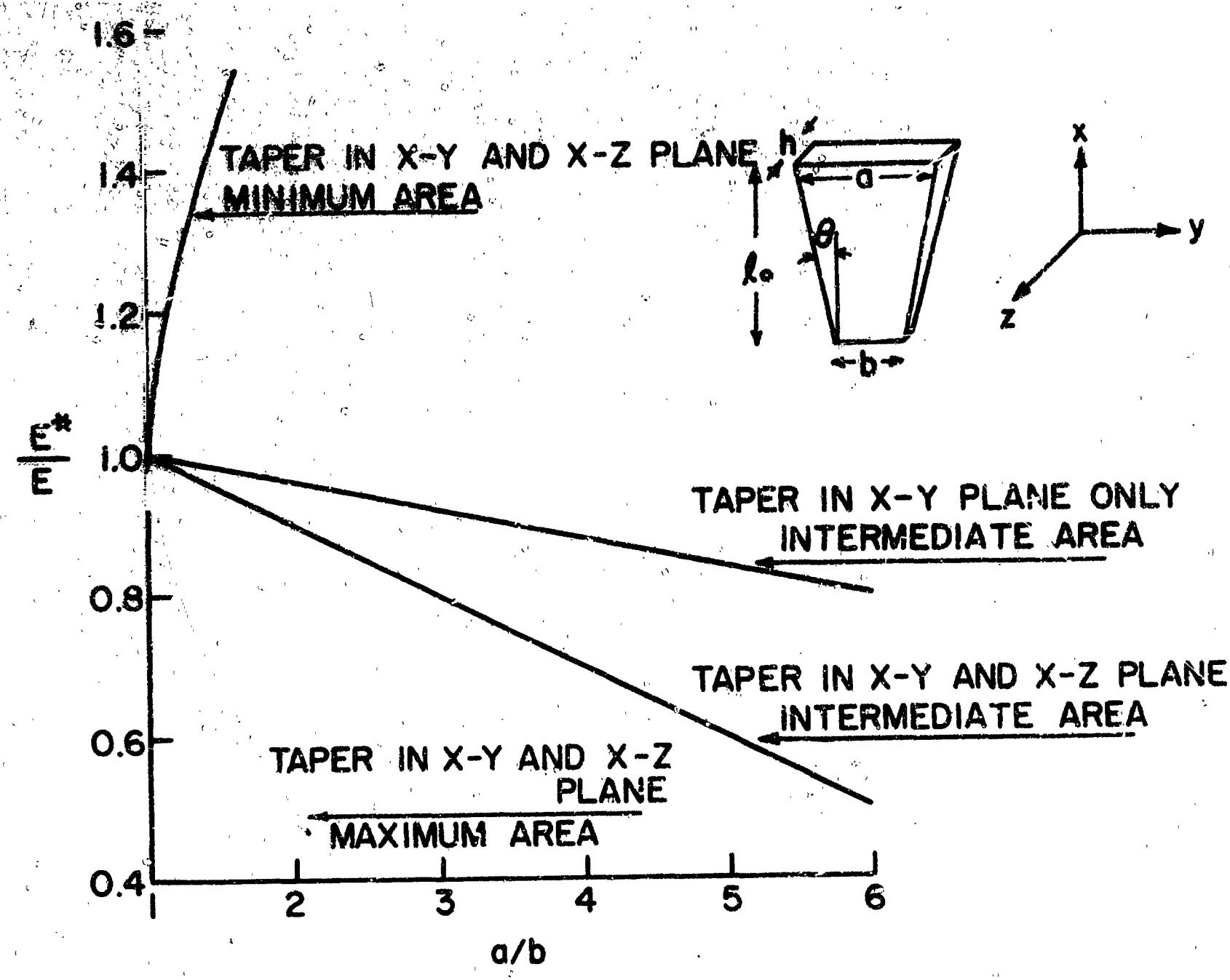

1.6
1.4
1.2
1.0
0.8
0.6
0.4
E*/E
TAPER IN X-Y AND X-Z PLANE
MINIMUM AREA
TAPER IN X-Y PLANE ONLY
INTERMEDIATE AREA
TAPER IN X-Y AND X-Z PLANE
INTERMEDIATE AREA
TAPER IN X-Y AND X-Z
PLANE
MAXIMUM AREA
1
2
3
4
5
6
a/b
h
a
θ
l₀
b
x
y
z

Figure B-1

APPENDIX C

EXPERIMENTAL TECHNIQUES

The following experimental techniques have been found to be useful in the characterization of B_4C whiskers. These techniques can of course be extended to many other small fibers.

I. X-RAY DIFFRACTION

1. Special specimen preparation techniques were developed to handle the small crystals (c.a. 10μ diameter, 100μ length) for x-ray diffraction analysis. It was found that very suitable 'rat-tail' specimens could be produced by rolling out or kneading a drop of Duco cement in which many whiskers had been embedded. The whiskers were picked up in the drop of cement by manipulating the drop over the inner surface of the tube on which the whiskers had been produced. The specimens so formed were examined in a cylindrical, powder x-ray camera.

2. The following method was found to be very satisfactory for handling and subsequently examining the short B_4C whisker sections (less than 0.5 mm long) which remained on the tensile tester grips. The short whisker fragments which were cemented onto the fused silica tensile grips with sym-diphenyl carbizide were first removed from the grips in an acetone bath. The fiber sections thus removed from the grips were then further washed in clean acetone and placed on a clean glass microscope slide. A small quantity of petroleum jelly was then placed on the tip of a fine (about 0.5 mm diameter) pyrex glass rod. The whisker section was carefully retrieved on the end of the glass rod tipped with petroleum jelly. The whisker was then manipulated so that its axis was roughly parallel to the glass rod. The glass rod and whisker combination was then positioned on the goniometer of a single crystal x-ray diffraction camera. The whisker was next properly oriented on the goniometer and finally photographed. All manipulations of the fiber during mounting were found to be best carried out under a low power binocular microscope.

II. ELECTRON DIFFRACTION (TRANSMISSION)

Specimens were very simply prepared by placing a standard copper electron microscope specimen screen, which had previously been coated with a commercial adhesive*, in contact with the surface upon which the whiskers had grown. Quantities of suitably thin (c.a. 1000Å thick) whiskers were collected in this manner and examined in an Hitachi HU-11 electron microscope by means of selected area diffraction (a transmission diffraction technique).

III. ELECTRON MICROSCOPY (REPLICATION OF WHISKER SURFACES)

A method for preparing surface replicas of fine B_4C whiskers - with cross sectional areas ranging between about $5\mu^2$ to $500\mu^2$ was developed. The specimen preparation method is as follows. A thin layer of cellulose acetate in acetone is spread uniformly on the inner face of the bottom piston of a conventional metallographic specimen embedding die. The whisker(s) of interest is positioned in the center of the piston, the die is filled with bakelite powder, assembled, pressured and heated in the manner which is standard in metallographic techniques. The cellulose acetate layer serves to hold the fiber(s) in position as well as to act as a cushion for the fiber(s) during pressing. After pressing and cooling, the die is opened and the specimen removed. The layer of cellulose acetate which is found to adhere to the bakelite mount may either be stripped mechanically or removed with acetone. The fiber(s) will then be found to be embedded in the bakelite with one face available for replication. A primary replica of the exposed face may then be prepared by any of the well known methods of replica preparation, e.g., cellulose acetate in acetone.

*For example, the adhesive which may be obtained from Ernest F. Fullam, Inc., Schenectady, N. Y. may be used.